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Geochemical Considerations for Managed Aquifer Recharge Implementation in Potable Reuse

CALIFORNIA
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STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Geochemical Considerations for Managed Aquifer Recharge Implementation in Potable Reuse

Prepared by:

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Abstract and Benefits

Abstract

Managed aquifer recharge (MAR) entails recharging water into an aquifer for future recovery or for environmental benefits, including restoring water levels in an overdrawn aquifer, preventing saltwater intrusion, and improving water quality. Utilities often employ spreading basins and/or injection wells when implementing MAR. MAR also supports many potable reuse applications. The physical and geochemical compatibility of recharge water, native groundwater, and minerals in the receiving aquifer significantly influence the success of a MAR facility.

This project advances the understanding and practice of MAR in potable reuse applications by addressing two major questions:

- what are the common challenges experienced during MAR operations for potable reuse, and
- what are the best practices and strategies to address the common MAR challenges to enable successful implementation of MAR and how can this information be effectively communicated to utilities interested in MAR for potable reuse?

This project will help water utilities understand physical and geochemical issues specific to geographic locations associated with developing and operating successful MAR facilities. A robust decision support framework and other tools have been developed to guide utilities in assessing physical and geochemical issues during the planning, design, construction, and commissioning phases of a MAR project, and ultimately during its operation.

Benefits

- MAR assists utilities with long-term water supply planning, helps achieve future reuse goals, and diversifies a utility's water supply portfolio.
- The project guides water utilities through all phases of a MAR project.
- The decision support framework assists troubleshooting common physical and geochemical challenges experienced implementing MAR.
- A user-friendly tool provides a centralized repository for relevant literature sources and tools to address common physical and geochemical considerations for MAR implementation.

Keywords: Managed aquifer recharge (MAR), water reuse, potable reuse, injection well, recharge basin, advanced water treatment (AWT), microfiltration (MF), reverse osmosis (RO), dissolved oxygen (DO), pH adjustment, geochemical reaction, clogging, metals mobilization, hydrous ferric oxide (HFO), cation exchange, ionic strength, clay swelling, clay dispersion, pyrite oxidation, siderite, fatal flaw analysis, geochemical modeling, PHREEQC, PHREEPLOT, MINTEQA2, Geochemist's Workbench, membrane filter index (MFI), bypass filter index (BFI).

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Acronyms and Abbreviations

µg/L	Microgram(s) per liter
µm	Micrometer
AACo	Anne Arundel County
ACH	Aluminum chloralhydrate
ADM	Acid digestible metals
ADWG	Australian Drinking Water Guideline
Al-salts	aluminum-salts
ARC	Albert Robles Center
As (III)	Arsenite
As (V)	Arsenate
ASR	Aquifer storage and recovery
AWT	Advanced water treatment
BAC	Biological activated carbon
BFI	Bypass filter index
CAVSARP	Central Arva Valley Storage and Recovery Project
CEC	Cation ion exchange capacity
CRS	Chromium reducible sulfur
CVWD	Carpinteria Valley Water District
DFT	Decision Framework tool
DHCV	Downhole control valve
DO	Dissolved oxygen
EDX	Energy dispersive x-ray
EPA	U.S. Environmental Protection Agency
ES&T	Environmental Science and Technology
fbg	Feet below grade
$FeCO_3$	Siderite
FeS_2	Pyrite
floc/sed	Flocculation/sedimentation
ft^2/d	Feet squared per day
GAC	Granular activated carbon
gpm	Gallon(s) per minute
HFO	Hydrous ferric oxide
HRSD	Hampton Roads Sanitation District
ICP-MS	Inductively couple plasma mass spectrometry
LBGWBA	Livermore Groundwater Basin Aquifer
LV	Leederville Aquifer

LVL	Leo J. Vander Lans Advanced Water Treatment Facility
m/L	Moles per liter
MAR	Managed aquifer recharge
MBI	Mid-Basin Injection
MDL	Method detection limit
Meq/L	Milli-equivalents per liter
MF	Microfiltration
MFI	Membrane filter index
mg/kg	Milligram per kilogram
mg/L	Milligram(s) per liter
MGD	Million gallon per day
MR	Migrating Recharge
NDMA	N-Nitrosodimethylamine
NGW	Native groundwater
OCWD	Orange County Water District
PAS	Potomac Aquifer System
pCi/L	Picocuries per liter
PMCL	Primary Maximum Contaminant Level
PO_4^{-1}	Phosphate
PRV	Pressure reducing valve
PWRF	Patuxent Water Reclamation Facility
Redox	Oxidation-reduction
Rehab	Rehabilitation
RO	Reverse osmosis
SCWD	Soquel Creek Water District
sec/L^2	Seconds per liter squared
SEM	Scanning electron microscopy
SMCL	Secondary Maximum Contaminant Level
SRC	SWIFT Research Center
SWIFT	Sustainable Water Initiative for Tomorrow
SWRCB	State Water Resources Control Board
TDS	Total dissolved solids
TMWA	Truckee Meadows Water Authority
TOC	Total organic carbon
TSS	Total suspended solids
TTHM	Total trihalomethane
TWCP	Tucson Water Clearwater Program
UF	Ultrafiltration
UIC	Underground Injection Control Program

UV	Ultraviolet
WC	Water Corporation of Western Australia, Australia
Wm Pt	Woodman Point
WRD	Water Replenishment District of Sothern California
WRF	The Water Research Foundation
XANES	X-ray adsorption near-edge spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
YG	Yarragadee Aquifer

Executive Summary

Managed Aquifer Recharge (MAR) describes the intentional recharge of water into a subsurface aquifer through a specially designed well or basin for future recovery or other environmental benefit. Potable reuse MAR involves treating wastewater effluent to national and state water quality standards using advanced water treatment (AWT) techniques for recharge of aquifer systems. Accordingly, MAR represents an indirect potable reuse strategy that has the potential to reduce saltwater intrusion, counteract land subsidence, replenish diminishing groundwater supplies, improve groundwater quality (depending on current water quality), and reduce current nutrient discharges to surface waters. MAR can assist utilities with long-term water supply planning and will play an important role in future water reuse goals for water utilities worldwide.

ES.1 Physical and Geochemical Challenges to MAR Projects

Recharging reclaimed water treated by AWT methods into aquifers through MAR basins and wells can present unique physical and geochemical issues. Even when the AWT effluent (recharge or recharge water), or groundwater in the receiving aquifer, meets all the Federal Primary and Secondary Maximum Contaminant Levels (PMCL and SMCL) and state water quality requirements, physical or geochemical challenges can emerge when recharging water into an aquifer composed of reactive metal-bearing minerals, potentially unstable clay minerals, dissolved gases, and saline groundwater, all conditions typical in aquifers composed of sands, sandstone, limestone, or fractured crystalline (igneous and metamorphic) rocks.

At present the literature provides no standard, concise descriptions for discussing the types of water involved with MAR operations. Accordingly, this report assigns the following terms to describe these water types:

- AWT effluent or other water entering basins or wells—recharge water or recharge.
- Native water contained in aquifer before MAR operations or reacting with injected water—groundwater or native groundwater (NGW).
- Recharge after entering aquifer through basins or wells—migrating recharge.

Challenges can be comprised of physical and chemical reactions that damage elements of the borehole and aquifer environment, including the basin surface and proximal subsurface, well screen, filter pack, borehole wall, and proximal aquifers spaces with solids, accumulating clays, and precipitating metals. All of these factors reduce permeability local to the wellbore or basin, and eventually lower the infiltration rate or injection capacity (injectivity) of the MAR facilities.

Although not strictly related to geochemical reactions, total suspended solids (TSS) entrained in recharge water impose a profound, and chronically debilitating influence on MAR operations. TSS originates from inadequately treated/filtered water, chemical precipitates formed downstream of the AWT processes, sediment and dirt deposited in the piping leading to the MAR facility, and corrosion of piping and metal treatment vessels.

Geochemical issues emerge through the interaction of recharge with minerals contained in an aquifer matrix. The chemical interactions of concern include damaging fresh-water-sensitive clays, precipitating or dissolving metal-bearing minerals, acid-base reactions, oxidation-reduction (redox) reactions that potentially release metals troublesome to injection activities (iron and manganese), or harmful to the aquifer (arsenic) and local groundwater quality. Additionally, the chemistry of constituents contained in the recharge can change through reactions with aquifer minerals. Several utilities have encountered redox conditions in aquifer systems including reduced metals in the NGW, and metal-bearing minerals in the aquifer matrix reduce nitrate found at harmless concentrations (<10 milligrams per liter [mg/L]) in the recharge to nitrite at concentrations exceeding the PMCL (1 mg/L).

When considering physical and geochemical issues that influence MAR operations, the following measures have proven critical to successfully operating a MAR facility:

- Establish an approach that advances the MAR project in phases starting with fatal flaws analysis relying on literature and existing data, field investigations, pilot testing, and ultimately permanent facility development.
- Evaluate how TSS in the recharge water can influence clogging in a MAR well or basin, specifically the relationship between TSS and MAR well injectivity or basin infiltration rate.
- Characterize relationship between TSS in recharge water and maintenance required to keep MAR system operating at desired capacity.
- Assess compatibility of recharge water with NGW regarding the ionic strength and cation chemistry of each water type.
- Identify AWT water quality parameters (e.g., pH, redox, ionic strength, alkalinity, nitrate, ortho-phosphate, etc.) that react with the NGW or aquifer minerals to produce undesirable results, compromising MAR operations, or releasing harmful constituents causing environmental concerns in the receiving aquifer.
- Identify measures for conditioning aquifer minerals in situ prior to starting MAR operations.
- Develop treatment measures that optimize the recharge water chemistry to passivate reactive aquifer minerals over the service life of the MAR facility.
- Alternatively, remove constituents from the recharge water that are reactive with aquifer minerals.

Based on the issues outlined above, the approach described by this report will help utilities in understanding the capacity of a MAR system along with benefits, problems, and potential technical challenges before investing significant capital funds in a MAR facility.

ES.2 Utility Participation

A critical characteristic of this project has entailed enlisting utilities in project development including reviewing interim deliverables along with obtaining case and anecdotal experience on geochemical issues during MAR operations. Utilities that participated in the project now operate or plan on operating MAR facilities in the future. Jacobs teamed with the following utilities as partners for the project:

- Orange County Water District (OCWD)

- Truckee Meadows Water Authority (TMWA)
- Tucson Water, Tucson, Arizona
- The Water Corporation of Western Australia (WC), Perth, Australia
- Water Replenishment District of Southern California (WRD)

A critical task for the project entailed developing a questionnaire that posed questions about physical and geochemical issues to utility operators in the United States and Australia. In addition to the above utilities partnering on the project, other utilities who completed the survey included:

- Anne Arundel County (AACo), Annapolis, Maryland
- Carpinteria Valley Water District, Carpinteria, California
- Hampton Roads Sanitation District (HRSD), Virginia Beach, Virginia
- Soquel Creek Water District, Santa Cruz, California
- Valley Water, Campbell, California
- Zone 7 Water Agency/Tri-10Valley Agencies, Livermore-Amador Valley, California

In completing the surveys utilities provided information on their recharge methods, receiving aquifers, facility capacities, water quality, geochemical issues, and the benefit(s) each utility realized from operating or planning a MAR facility.

ES.3 Project Framework

The project organization involved a simple framework designed to benefit utilities in planning and operating MAR facilities and included the following tasks:

1. **Task 1: Literature Review:** Identify publications in the technical and scientific literature that describe physical and geochemical issues at MAR facilities and how utilities or researchers addressed the challenges.
2. **Task 2: Survey Utilities that Operate MAR facilities:** Worked with the project's utility partners to determine physical and geochemical issues most relevant to MAR facilities and how these issues are handled.
3. **Task 3: Framework Development:** Developed Microsoft Excel-based Decision Framework tool (DFT) that supports utilities in addressing clogging and geochemical issues experienced during their efforts in developing and operating MAR facilities.
4. **Task 4: Final Deliverables:** Prepared project deliverables in the form of annotated bibliography, summary of utility survey results, memoranda, and a final framework report.

ES.4 Project Objectives

The project team implemented the project based on the following objectives:

1. Determine the influence of geochemical reactions on regulated and unregulated geogenic contaminants
2. Identify important recharge water quality parameters involved in reactions

3. Develop criteria for optimizing recharge water quality
4. Characterize and develop methods to minimize TSS loading
5. Guide utilities in:
    a. Aquifer selection
    b. Assessing geochemical compatibility
    c. Pretreatment techniques for recharge
    d. Long-term monitoring techniques

ES.5 Report Organization

This report includes the following sections:

- Chapter 1—Introduction
- Chapter 2—Literature Review
- Chapter 3—Utility Survey
- Chapter 4—Framework Development
- Chapter 5—Conclusions and Recommendations
- Appendix A—Literature Review Summary
- Appendix B—Utility Survey Methodology
- Appendix C—Testing the Decision Framework using Utility Survey Responses
- Appendix D—Decision Framework Tool
- References

ES.6 Literature Review

ES.6.1 Objectives

The first task for the project involved conducting a comprehensive literature review. The intent of the literature review involved identifying publications in the technical and scientific literature that describe physical and geochemical issues at MAR facilities, and how utilities addressed these challenges to provide a linkage between the body of literature and the decision support framework.

In developing the literature review, the project team constrained the search to how the topics and subtopics for the literature review related to potable reuse MAR applications. An enormous number of publications deal with similar topics, but only distantly correspond to MAR applications and thus fall outside the scope of the review. Thus, developers of this review included select, classic publications that may enrich the utility of the publications list.

The literature review was thorough, current, and ongoing throughout this research project. This review emphasized issues requiring ongoing research, developing technology, and new approaches to addressing geochemical issues in situ. Results of the research strengthen the applicability of the decision support framework developed for the project.

ES.6.2 Methods

For the literature review, the project team compiled various sources devoted to geochemical issues experienced during MAR. The list of sources includes published papers, textbooks, proceedings, conference presentations, studies, articles etc. An annotated bibliography, found in Appendix A, is organized alphabetically by topic, contains the citation, and includes a high-level abstract for each literature source.

ES.7 Utility Survey

ES.7.1 Survey Overview

The second task for the project involved creating and soliciting an extensive utility survey. The primary objective of the survey was to obtain important information relevant to MAR facilities and to gain a deeper understanding for the types of challenges faced and the solutions utilities have developed to overcome these issues. Appendix B contains information on the approach and methodology used in the utility survey.

ES.7.2 Utilities Responding to Surveys

Twelve utilities responded the project survey, reporting on seven operating MAR facilities and seven facilities in various stages of planning. Three participants including the WC in Australia, WRD in Los Angeles County, California, and TMWA in Reno, Nevada, operate MAR facilities and have plans for developing separate facilities, or significantly expanding existing facilities using different technologies, like adding wells to a facility that relies on basins. The HRSD in Virginia operates a 1.0 million gallon per day (MGD) research facility while planning to develop MAR at four different locations, with a capacity exceeding 100 MGD.

This chapter briefly describes each operating MAR facility and those in planning. Sections describe facility capacities, type of recharge facility (basin/wells), aquifer lithologies, the geochemistry of recharge, groundwater, and if appropriate, migrating recharge. Sections also discuss operational issues related to clogging and problems utilities have faced involving geochemical reactions. Information provided in this chapter relies on the thoroughness and care taken by utilities in completing the surveys.

ES.7.3 Summary of Survey Geochemical Results

Utilities responding to the project's survey displayed marked geochemical similarities. All the participants operate MAR facilities or plan to operate facilities that recharge to sand or sandstone aquifers. Although aquifers composed of carbonate (limestone and dolomite) and vesicular extrusive igneous rocks occur throughout the United States and worldwide, none of the utilities involved in the project employ these types of aquifer for MAR.

All the recharge waters contained near saturated concentrations of dissolved oxygen (DO). Thus, recharge will likely alter redox conditions in the receiving aquifers. Moreover, DO can react directly with reactive metal-bearing minerals in the aquifer that control the chemistry of the migrating recharge by lowering its pH, nitrate, and alkalinity, while increasing concentrations of metals and other constituents including sulfate and carbonate.

Otherwise, recharge consisted of two chemistry types, based on the AWT treatment processes. Recharge treated with membranes displayed low concentrations of total dissolved solids (TDS), often significantly below 100 mg/L and a sodium—chloride chemistry. In contrast, recharge treated using non-membrane processes displayed more elevated TDS concentrations often exceeding 500 mg/L. Recharge from non-membrane processes produced a range of ionic chemistry including sodium—chloride, mixed cation—bicarbonate and mixed cation—sulfate.

Ionic strength and chemistry represent important considerations for MAR facilities. Ionic strength, reported in moles per liter (m/L) is a function of all ions present in a solution, measuring the concentration of all ions scaled for each type of ion by its charge. The parameter becomes important when the ionic strength of the groundwater exceeds the recharge by more than an order of magnitude. Introducing a low ionic-strength recharge water into an aquifer displaces groundwater containing positive charges away from negatively charged clay mineral surfaces creating a repulsive environment. Clay minerals disperse, swell, fragment, and migrate with the groundwater flow.

Dispersing clays represent a special type of formation damage. Migrating clays can accumulate in pore throats (brush pile), clogging the flowpath and reducing aquifer permeability. Formation damage occurs rapidly, severely lowers permeability, and usually proves irreversible when applying conventional rehabilitation methods to basins or wells. Less commonly, the ionic strength of groundwater can fall below that of the recharge water. The relationship becomes a concern if a single prevailing cation in the recharge exhibits greater concentrations than the others. An as example, elevated sodium in recharge can cause formation damage in a clastic aquifer containing low ionic-strength groundwater.

Common cations, including calcium, potassium, magnesium, and sodium, in recharge water can influence how recharge reacts with clay minerals occupying the interstices of sands or sandstone aquifers. Exchanging cations between the recharge water and interstitial clays can create another type of formation damage if the reactions damage the clay mineral edge, cause it to fragment, migrate, and eventually brush pile in pore throats. Differing dominant cations in the recharge and groundwater often indicate a potential for exchange reactions during MAR operations.

Except for the HRSD and the WC’s Woodman Point locations, most groundwater displayed concentrations of TDS consistent with fresh water, typically less than 600 mg/L. TDS at HRSD’s Sustainable Water for Tomorrow (SWIFT) SWIFT Research Center (SRC) and WC’s Woodman Point fell in the brackish range varying between 1,600 and 5,500 mg/L. In addition, groundwater at several of HRSD’s SWIFT localities displayed TDS concentrations approaching 25,000 mg/L. Invariably, a utility recharging water under these conditions should condition clay minerals before conducting injection testing or simulating MAR operations with fresh AWT effluent or potable water. Flushing fresh water into a brackish environment reduces positive charges around clay minerals, causing them to swell, disperse and start migrating in the aquifer.

Conversely, Tucson Water and AACo now or will recharge water displaying a higher TDS and ionic strength than the groundwater, however both recharge and groundwater remains in the fresh category. In these situations, newer systems should look closely at the difference in sodium concentrations. High sodium concentrations in the recharge can fragment the edges of clay minerals which initiates migration and eventually accumulation (brush piling) of the fragments. The fragments block pore throats damaging aquifer permeability. Although happening on a microscopic scale the problems develop rapidly and proves irreversible, diminishing injectivity to a fraction of its original index.

Several facilities reported geochemical issues during MAR operations involving the appearance of deleterious constituents at nearby monitoring wells. These issues included the arsenic, cobalt, iron and manganese mobilization, nitrite production and elevated total trihalomethanes (TTHMs) appearing in local monitoring wells.

Also, utilities have reported problems related to basin and well clogging through mechanical (siltation), biological (biofouling), and minerals precipitation mechanisms. Basin operators typically handle clogging by annual maintenance including surface ripping and occasional sediment removal. By comparison, wells create greater complexity regarding maintenance. OCWD, the oldest and largest operator of MAR wells, has developed several innovative yet uniform techniques for maintaining their large network of wells.

ES.8 Framework Development

Utilities can employ many approaches in evaluating potential physical and geochemical issues anticipated when applying potable reuse for MAR to basins or wells. Most utilities apply a phased approach organizing MAR projects into the following:

- Phase 1 Geochemical Compatibility Investigation for MAR Projects
- Phase 2 Geochemical Field Investigation
- Phase 3 MAR Facility Start Up and Operations from Geochemical Perspective

The Decision Framework hinges on the three project phases portrayed in primary flowcharts comprising easy to follow pathways. Phase 1 encompasses a fatal flaws analysis that employs data available from the utilities files or literature sources to determine the viability of MAR in an area, site, or specific aquifer(s). The pathways often terminate at nodes that refer the user to secondary flowcharts or salient literature addressing specific geochemical or well/basin clogging issues. Most of secondary charts offer the user several pathways to a solution, while others describe a restrictive path to solving an issue.

ES.8.1 Introduction

A Phase 1 Geochemical Compatibility Investigation MAR Project (Phase 1) involves a study aimed at seeking critical problems that may render a potential MAR project infeasible. In this section, fatal flaws may entail geochemical reactions that appear too difficult to manage through in situ techniques or any number of other problems involving geochemistry or well/basin clogging or permutations thereof that can combine to render a project infeasible. Just as important, other Phase 1 activities include selecting the receiving aquifer(s), estimating the injection capacities of basins and wells, identifying recharge and groundwater quality characteristics.

Phase 1 studies usually rely on existing data from multiple sources along with rudimentary field activities, if necessary. Thus, Phase 1 studies do not typically require extensive drilling, sampling, or testing, however, if no fatal flaws emerge, the study uncovers data gaps that a field investigation can address during a Phase 2 Field Investigation (Phase 2).

A Phase 2 investigation entails conducting a field investigation that characterizes the geologic, hydrogeologic, and geochemical characteristics of the storage aquifer. The process nearly always comprises but does not limit the investigation to the following activities:

- Collecting formation samples in the form of drill cuttings or core
- Obtaining mineralogical analysis of the formation samples
- Performing bore- and surface geophysical surveys
- Conducting batch or bench-scale tests with formation samples and recharge water (recharge)
- Drilling, installing, and developing test and observation wells
- Conducting pumping tests, including step drawdown and constant rate tests
- Conducting injection tests
- Collecting water quality samples of groundwater and recharge, if available

By completing the type of Phase 2 investigation outlined above the utility can build a strong understanding of geologic, hydrologic, and geochemical characteristics of the test site. Moreover, testing during the field investigation enables developing design criteria for constructing a permanent MAR facility including recharge wells and basins, AWT needs, monitoring systems, aquifer conditioning, etc., for implementation during Phase 3.

Phase 3 MAR Operations (Phase 3) usually consists of designing, permitting, constructing the MAR facility and ultimately operating the facility, and thus represents, by far the phase lasting the longest. Fortunately, identification of most physical and geochemical issues that can affect MAR operations occur during Phases 1 and 2. Still, several issues remain unresolved into Phase 3 particularly if construction of the AWT happens coincident with Phase 3 activities. Thus, although simulated recharge quality can support simulating geochemical reactions, the most accurate simulations originate from actual recharge chemistry. Just as important, operators cannot evaluate the clogging potential of the recharge before commissioning the AWT.

Chapter 4 discusses the framework of a potable reuse MAR project and how a utility can identify important clogging or geochemical reactions during each project phase. Chapter 4 describes how to navigate the contents of the Excel-based, DFT, developed to guide utilities through issues related to undesired geochemical reactions and basin/well clogging. The Excel-based DFT steps users through a series of questions related to Phase 1, Phase 2, and Phase 3 MAR evaluations and provides resources based on the selected inputs. The intended outcome of the tool is to provide utilities with an additional resource to help them evaluate potential physical and geochemical issues anticipated when applying potable reuse for MAR to basins and wells.

ES.8.2 Objectives

The objectives of Chapter 4 include:

- Guiding utilities in selecting the best aquifer(s) for MAR operations from a geochemical perspective.
- Assessing the geochemical compatibility between recharge, groundwater, and aquifer mineralogy and amorphous phases.
- Determining the need for aquifer conditioning prior to starting MAR operations.
- Resolving whether recharge water requires pretreatment to passivate potential deleterious reactions in situ.
- Selecting the best pretreatment measures depending on recharge chemistry and aquifer mineralogy.
- Long-term well performance monitoring.
- Long-term monitoring of recharge migrating in the aquifer.

The section steps the user through the MAR Project Phases while discussing which phases identify the important geochemical reactions and clogging issues. Project phases form the essential baseline for branching off into geochemical reactions. Accordingly, Project Phases 1 through 3 form the basis for sections in Chapter 4.

ES.8.3 Conventional Geochemical Analysis

Despite the variety of activities assigned to each project phase, from a geochemical perspective, all three phases involve conventional geochemical analysis and geochemical modeling. Conventional geochemical analyses comprise applying statistical, graphing, and plotting techniques using the recharge and groundwater chemistry, and to the extent practical, mineralogy.

- Techniques used in describing predominant ionic species and the relationship between samples involve:
  1. Piper Diagrams
  2. Stiff Diagrams
  3. Cation ratios

- Analysis of the redox potential of water samples comprise:
  1. Redox diagrams
  2. Redox Constituent Analysis

- Assessing the stability of clays and metal-bearing minerals (iron, manganese, aluminum, arsenic, etc.) in the receiving aquifer(s) will employ the following techniques:
  1. Parametric statistics
  2. Correlation Coefficients
  3. Regression Analysis
  4. Predominance Area Diagrams
  5. Phase Diagrams

Redox line diagrams and the Jurgens et al. (2009) redox constituent analysis help describe redox conditions in the aquifer based on aqueous analysis. These techniques become particularly important when considering (for example) the mobility of metals in the receiving aquifer(s) under changing redox conditions caused by an oxygen-rich recharge water. Under the circumneutral pH conditions found in most aquifers, redox controls the mobility of iron, manganese, and arsenic, and the characteristics of adsorptive mineral surfaces that can hinder their mobility.

Phase diagrams provide a powerful tool for assessing aqueous and mineral equilibria during Phase 1 studies. The diagrams facilitate plotting the path traversed between dissolved ions and minerals during storage in an aquifer.

ES.8.4 Geochemical Modeling

Utilities will typically use geochemical models during every phase of a MAR project. During all phases, models have proven particularly useful in simulating the following reactions and chemical relationships:

- Reactions between recharge water, native groundwater, and aquifer mineralogy.
- Aquifer conditioning techniques to stabilize minerals or amorphous phases in situ.
- Long-term changes in the redox, acid-base, clay chemistry, etc. environment during MAR operations.
- Speciating ions and complexes.
- Developing saturation indices for potential mineral phases.
- Calculating ionic strengths of aqueous samples.
- Calculating activities of constituents for plotting phase diagrams.

Geochemical modeling helps identify the potential presence of minerals from a groundwater quality analysis, or not detected in x-ray diffraction or petrographic analysis conducted during later phases of a MAR project. Many minerals can go undetected because of their lack of crystallinity (amorphous phases), or because lithologic sampling does not cover every depth interval of the aquifer section. Moreover, amorphous minerals often reside in the interstitial spaces of aquifers. Consequently, these phases display a high degree of reactivity, thus, controlling groundwater or recovered water chemistry.

ES.9 Conclusions

The project entailed characterizing the unique physical and geochemical issues encountered by utilities when planning, testing, or operating MAR systems. To constrain the scope of the project, the technical evaluation was limited to basins or wells receiving recharge purified to drinking water standards using AWT methods. Conceptually, the approach eliminated aquifer storage and recovery (ASR) or facilities that rely on storm or reclaimed wastewater as the source of recharge, yet some MAR facilities recharge a combination of AWT effluent, reclaimed water, stormwater or treated surface water.

Work performed for the project helped developed the following conclusions:

- Although utilities conduct MAR operations in all types of aquifers including carbonate rocks and even crystalline rocks displaying primary porosity like vesicular, extrusive igneous rocks, the project's utility partners, and most journal publications describe MAR operations in sand and sandstone aquifers.

- Clogging by particulates entrained in recharge, although not a strictly geochemical process, seemed to influence MAR operations in basins and wells at all the facilities evaluated for this project.
- Mitigating clogging in basins entails periodic drying and scraping with occasional sediment removal.
- With the well bore exemplifying a significantly smaller surface area than the infiltration area of a basin, MAR wells show greater sensitivity to clogging by solids. As operators cannot visually observe clogging in MAR wells, they must remain vigilant through other methods like tracking injection levels, injectivities and the results from membrane filter index (MFI) testing to determine maintenance frequencies.
- Recent research in ASR and MAR wells show that recharge displaying MFI indices exceeding 3 seconds per liter squared (sec/L^2) prompts greater maintenance frequency for MAR wells including periodic backflushing and invasive well rehabilitation. Accordingly, the Decision Framework developed for this project relies on the MFI index to provide quantitative thresholds in recommending maintenance frequencies for MAR wells.
- Geochemical issues like clay dispersion can influence the operating characteristics of MAR facilities while metals mobilization in migrating recharge influences water quality in the aquifer and thus, the environmental viability of a MAR project.
- Recharging fresh water into an aquifer containing brackish or saline groundwater can cause clay dispersion and migration if the ionic strength of the groundwater exceeds the recharge by one order of magnitude.
- In fine or medium grained sand or sandstone aquifers, ASR, MAR and other injection-type wells have suffered catastrophic, irreversible permeability losses (formation damage) when recharging water of significantly lower ionic strength than the native groundwater.
- In coarser-grained aquifers displaying larger pore spaces with strong connectivity, clay dispersion may not present as great an issue. As an example, utilities in Southern California utilities have recharged fresh water into brackish aquifers to prevent saltwater intrusion since the 1960s with no evidence of formation damage.
- The Decision Framework, narrative in the report and Case Studies provided in Appendix C all describe how a utility can take the proper measures to prevent formation damage.
- Of the utility partners, only one operating facility has implemented these measures or shown the recharge and groundwater conditions requiring measures to prevent clay dispersion. However, several facilities currently in planning should consider implementing these measures.
- Several facilities displayed issues with releasing cationic metals from reactive aquifer minerals during MAR operations. Typically, samples of migrating recharge at nearby monitoring wells displayed geochemical evidence of pyrite oxidation like declining pH and alkalinity and increasing sulfate along with the release of iron, manganese, cobalt, nickel, or zinc.
- The Decision Framework provides measures for treating reactive minerals in situ including pH adjustment, oxidant addition, and raising the buffering capacity of migrating recharge. These actions precipitate hydrous ferric oxide (HFO) surfaces that passivate reactive mineral

surfaces, while building an adsorptive surface displaying a high affinity for fixing cationic metals.

- Conditioning aquifers to preclude clay dispersion or pretreating recharge to mitigate the release of cationic metals represent relatively straightforward solutions to the respective issues. By contrast, applying in situ measures to prevent the release of arsenic from minerals or metal oxide surfaces can involve complicated combinations of measures depending on the ionic state of arsenic, redox conditions in groundwater and recharge, the presence of dissolved oxygen, and the presence of competitive anions like phosphate or carbonate in recharge.
- As an example, removing dissolved oxygen from recharge has proven effective at preventing pyrite oxidation and the subsequent release of arsenic. However, pyrite does not always represent the source of arsenic in an aquifer. Arsenic often adsorbs to metal oxide surfaces. So, removing DO from recharge may enhance reductive dissolution of metal oxide surfaces fixing arsenic in the aquifer, releasing arsenic into migrating recharge.
- The Decision Framework developed from the work of others and the authors of the report, and provides multiple pathways for handling arsenic in situ, yet remains an unfinished work that will require augmenting over years of upcoming MAR operations.
- Although several utilities have operated MAR facilities for many years, the practice still appears relatively new and shows signs of growing rapidly worldwide. Thus, Water Research Foundation should consider revising the work performed for the project periodically to reflect recent advances in technology and techniques for handling complex geochemical issues.

ES.10 Related WRF Research

- Compiling Evidence of Pathogen Reduction through Managed Aquifer Recharge and Recovery (4957)
- Enhancing the Soil Aquifer Treatment Process for Potable Reuse (1699)
- Role of Retention Time in the Environmental Buffer of Indirect Potable Reuse Projects (1671)
- Soil Aquifer Treatment Characterization with Soil Columns for Groundwater Recharge in the San Fernando Valley (4600)
- Groundwater Replenishment with Recycled Water on Agricultural Lands in California (4782)

CHAPTER 1

Introduction

Managed Aquifer Recharge (MAR) describes the intentional recharge of water into a subsurface aquifer through a specially designed well or basin for future recovery or other environmental benefit. Potable reuse MAR involves treating wastewater effluent to national and state water quality standards using advanced water treatment (AWT) techniques for recharge of aquifer systems. Accordingly, MAR represents an indirect potable reuse strategy that has the potential to reduce saltwater intrusion, counteract land subsidence, replenish diminishing groundwater supplies, improve groundwater quality (depending on current water quality), and reduce current nutrient discharges to surface waters. MAR can assist utilities with long-term water supply planning and will play an important role in future water reuse goals for water utilities worldwide.

Several utilities that now operate or plan to construct, commission and operate MAR facilities have agreed to participate in the project (Figure 1-1). They provided vital information on their operations and planning through utility surveys, interviews, and informal discussions. Moreover, many have reviewed and added narrative, figures, and tables to this report.

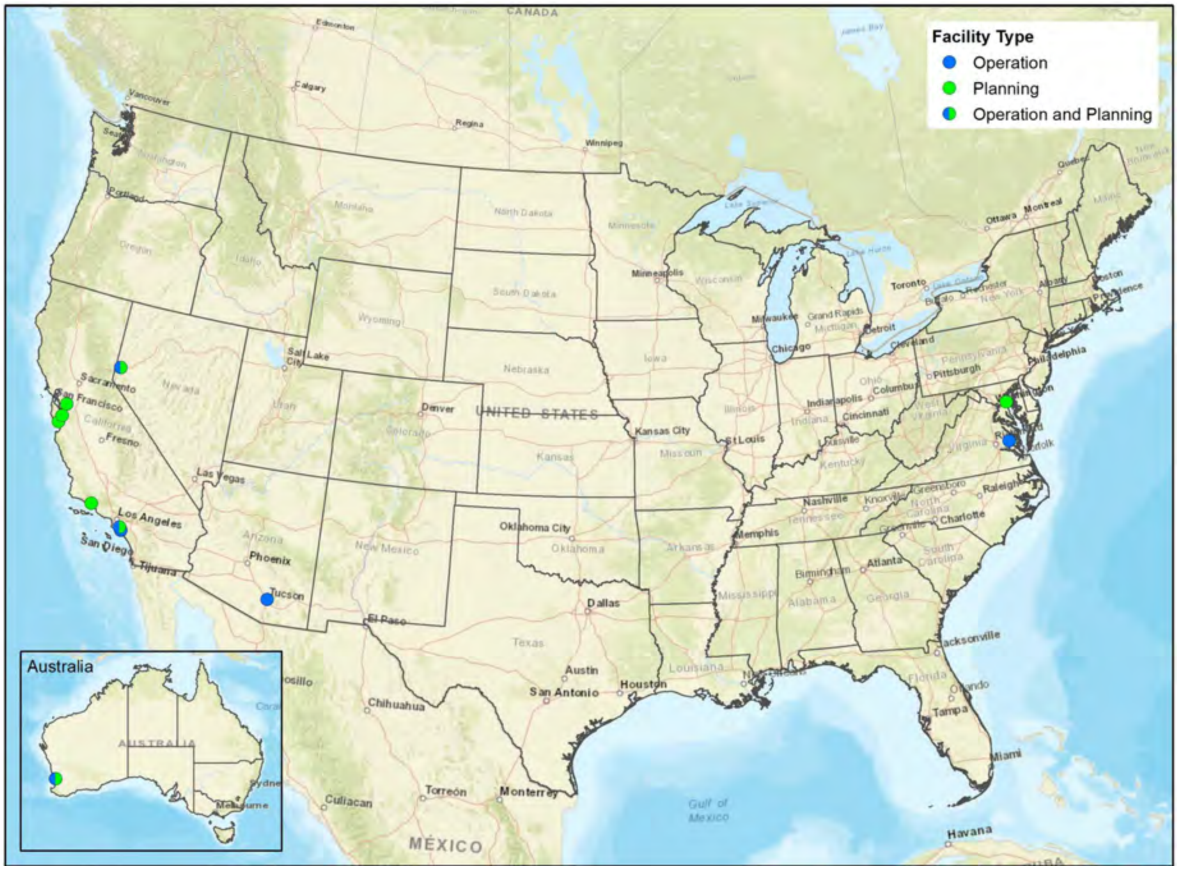


Figure 1-1. Utility Survey Participants Facility Locations.

1.1 Physical and Geochemical Challenges to MAR Projects

Recharging reclaimed water treated by AWT methods into aquifers through MAR basins and wells can present unique physical and geochemical issues. Even when the AWT effluent (recharge or recharge water), or groundwater in the receiving aquifer, meets all the Federal Primary and Secondary Maximum Contaminant Levels (PMCL and SMCL) physical or geochemical challenges can emerge when recharging water into an aquifer composed of reactive metal-bearing minerals (Figure 1-2), potentially unstable clay minerals, dissolved gases, and saline groundwater, all conditions typical in aquifers composed of sands, sandstone, limestone, or fractured crystalline (igneous and metamorphic) rocks.

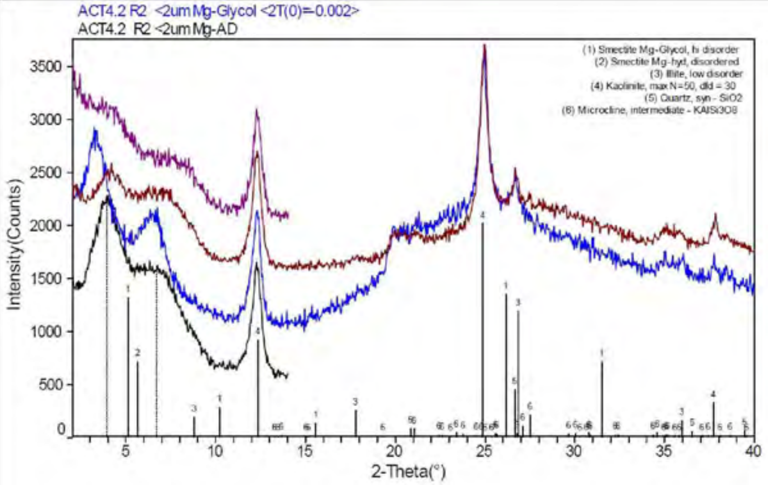
At present the literature provides no standard, concise descriptions for discussing water involved with MAR operations. Accordingly, this report uses the following terms to describe these water types:

- AWT effluent or other water entering basins or wells—recharge water or recharge.
- Native water contained in aquifer before MAR operations or reacting with injected water—groundwater or native groundwater (NGW).
- Recharge after entering aquifer through basins or wells—migrating recharge.

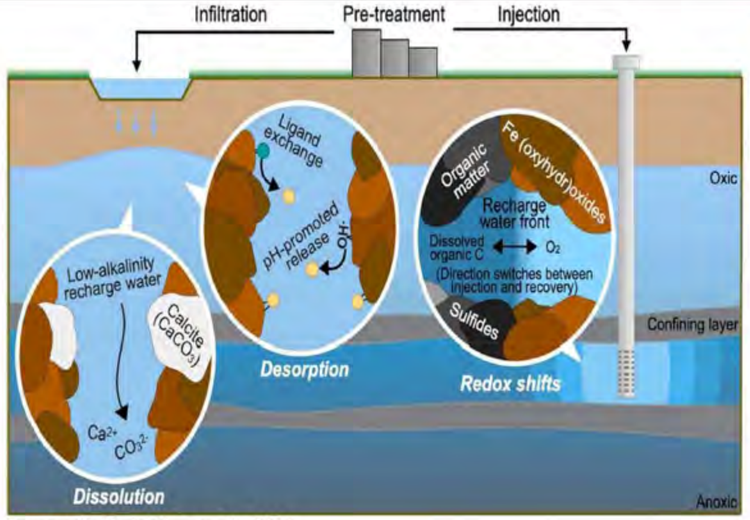
Challenges can be comprised of physical and chemical reactions that damage elements of the borehole and aquifer environment, including the basin surface and proximal subsurface, well screen, filter pack, borehole wall, and proximal aquifers (Figure 1-2). Damage can ensue by clogging pore spaces with solids, accumulating clays, and precipitating metals, all factors that reduce permeability local to the wellbore, and eventually lower the injection capacity (injectivity) of the MAR facilities.

Although not strictly related to geochemical reactions, total suspended solids (TSS) entrained in recharge water impose a profound, and chronically debilitating influence on MAR operations. TSS originates from inadequately treated/filtered water, chemical precipitates formed downstream of the AWT processes, sediment and dirt deposited in the piping leading to the MAR well, and corrosion of piping and metal treatment vessels. As an example, Orange County Water District (OCWD) has found that corrosion of piping produces TSS in their MAR wells and can be a significant factor in diminishing injection specific capacity (injectivity). Some of OCWD's MAR wells feature relatively short screen segments (10 to 40 feet) distributed over a single long/deep multi-aquifer casing string (Figure 1-3), so these discrete intervals can clog when the recharge water entrains TSS from pipeline corrosion.

In colder regions, lower recharge temperatures in winter can seasonally compromise MAR operations. Reaching its maximum viscosity at 4 degrees Celsius, colder water reduces the intrinsic permeability of any media the recharge flows through, including sandy aquifers. Also, colder, more viscous water (Brown and Silvey 1977) follows the most permeable pathways through an aquifer, precluding dispersion of recharge into less permeable areas of the aquifer where reactive minerals typically reside. Thus, cold recharge-containing agents used for conditioning minerals in situ, may not contact minerals located off the main flowpaths in the aquifer.

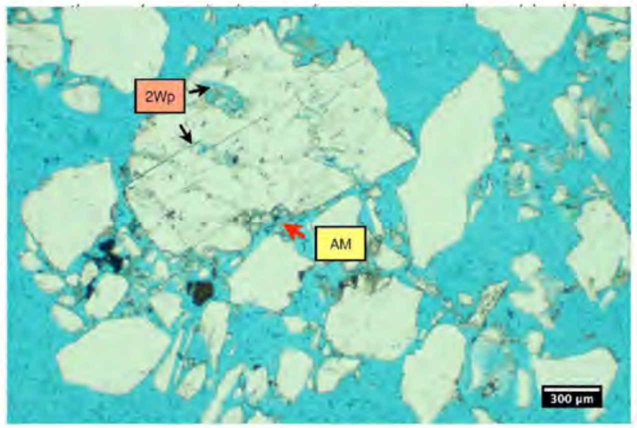


Cation Exchange
Shown on X-ray Diffractogram



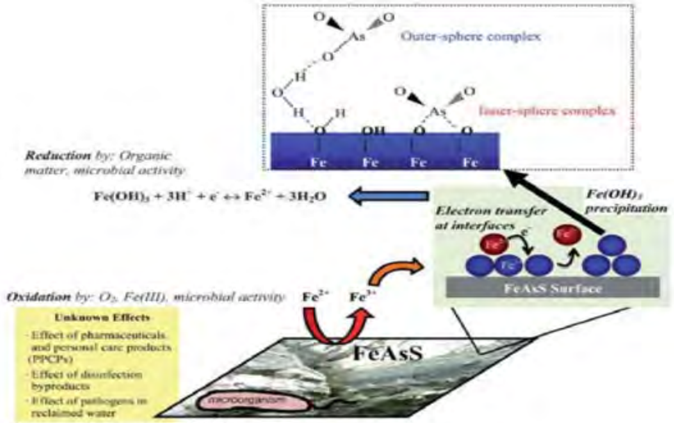
Source: Fakhreddine et. al., 2021

MAR Geochemical Environments



Feldspar Dissolution and and Migration of Clay Weathering Products

Reactive crystalline and framboidal pyrite leach iron, manganese, and arsenic into migrating recharge.

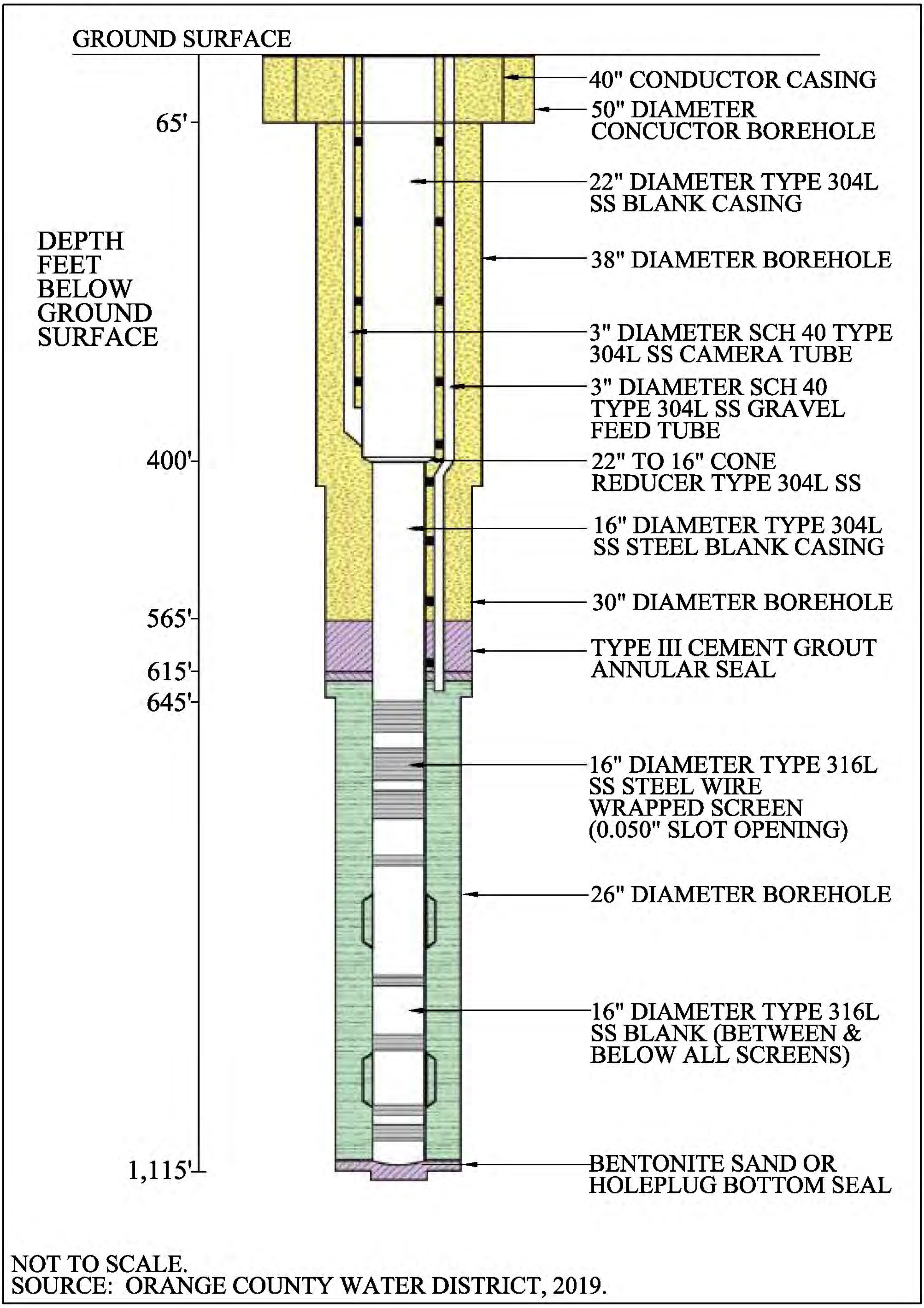


Source: Neil et. al., 2012

Arsenic Mobilization

DEN001 | DOCUMENTS - DEN1 WBG IMPERIAL SF | \DESIGNS - SMALL PROJECTS | W9Y30400 - WRF MAR IMP IN POTABLE REUSE | DLV | F32_W9Y30400.dgn

Figure 1-2. Geochemical Reactions Common to MAR Operations.



SOURCE: ORANGE COUNTY WATER DISTRICT, 2019.

Figure 1-3. OCWD Conceptual MAR Well Design.

Geochemical issues can emerge through the interaction of recharge water with minerals contained in the aquifer matrix. The chemical interactions of concern include damaging fresh-water-sensitive clays, precipitating or dissolving metal-bearing minerals, acid-base reactions, oxidation-reduction (redox) reactions that potentially precipitate metals that diminish injectivity (iron and manganese), or are harmful to the aquifer (arsenic), human health of end users of aquifer water, and groundwater-dependent ecosystems. Additionally, the chemistry of constituents contained in the recharge water can change through reactions with aquifer minerals prompting reactions often unique to a single or a small number of facilities. As an example, metal-bearing minerals in the aquifer matrix can reduce nitrate found at harmless concentrations (less than 10 milligrams per liter [mg/L]) in the recharge to nitrite at concentrations exceeding the PMCL (1 mg/L) in migrating recharge.

When considering physical and geochemical issues that influence MAR operations (Figure 1-4), the following measures have proven critical to successfully operating a MAR facility:

- Evaluate how TSS in the recharge water can influence clogging in a MAR well, specifically the relationship between TSS and MAR well injectivity.
- Characterize relationship between TSS in recharge water and maintenance required to keep MAR system operating at desired capacity.
- Determine if recharge water temperature represents an issue of concern for MAR operations.
- Assess compatibility of recharge water with NGW regarding the ionic strength and cation chemistry of each water type. MAR and water flooding (petroleum) projects have demonstrated that recharging water exhibiting a lower ionic strength by one order of magnitude (Gray and Rex 1966), compared to the NGW can swell and/or disperse clays, irreversibly reducing the permeability of the receiving aquifer. Similarly, differing cationic chemistry can also alter interstitial clay minerals and reduce aquifer permeability (Brown and Silvey 1977, Torkzaban, et al. 2015a, and Torkzaban, et al. 2015b).
- Identify AWT water quality parameters (e.g., pH, redox, ionic strength, alkalinity, nitrate, ortho-phosphate, etc.) that react with the NGW or aquifer minerals to produce undesirable results, compromising MAR operations, or releasing harmful constituents causing environmental concerns in the receiving aquifer.
- Identify measures for conditioning aquifer minerals in situ prior to starting MAR operations, like stabilizing interstitial clay minerals in the sensitive area immediately around a MAR wellbore (Holloway, et al. 2018).
- Develop treatment measures that optimize the recharge water chemistry to passivate reactive aquifer minerals over the service life of the MAR facility.
- Alternatively, remove constituents from the recharge water that are reactive with aquifer minerals. In Florida, aquifer storage and recovery (ASR) and MAR facility operators remove dissolved oxygen (DO) and/or residual oxidants from the recharge water to preclude oxidizing the sulfide mineral, pyrite, and releasing arsenic into the stored water (ENTRIX 2012). Moreover, removing phosphate prevents it from competing with other oxy-anions adsorbed the metal oxide surfaces.

- Establish an approach that advances the MAR project in phases starting with fatal flaws analysis relying on literature and existing data, field investigations, pilot testing, and ultimately permanent facility development. The approach will help utilities in understanding the capacity of a MAR system along with benefits, problems, and potential technical challenges before investing significant capital funds in a MAR facility.

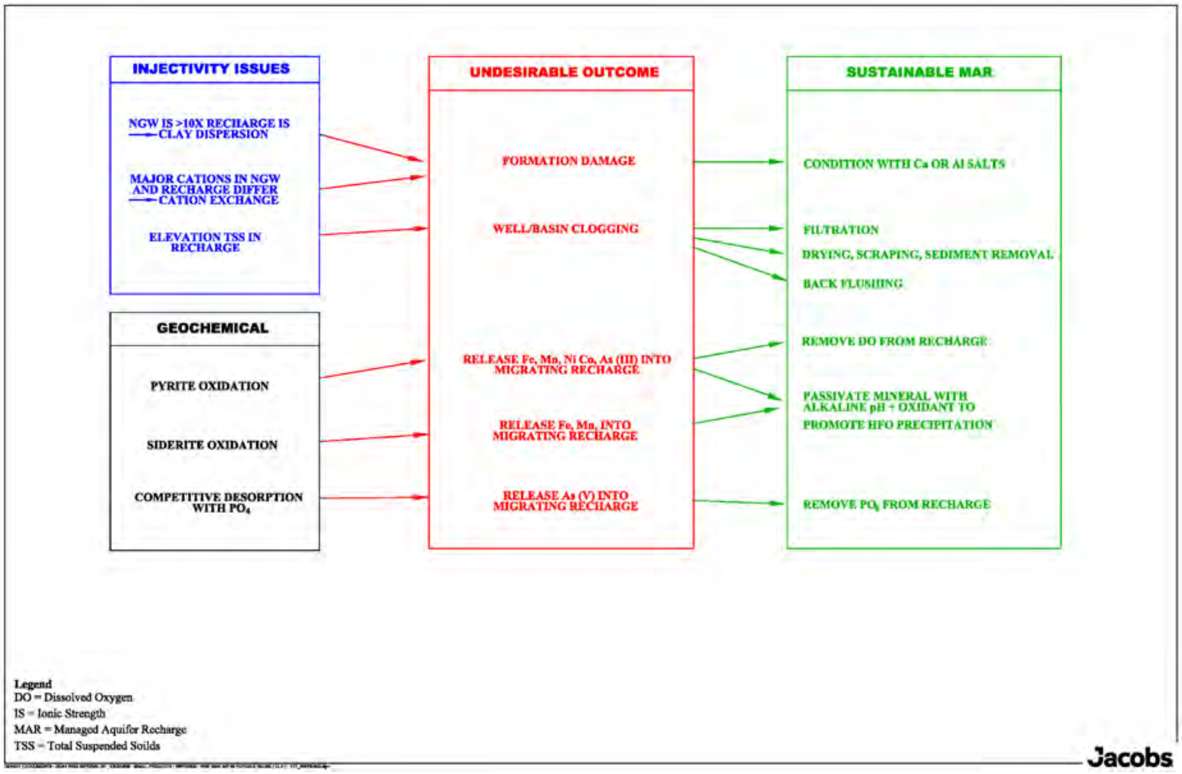


Figure 1-4. Relationships Between Geochemical Reactions Injectivity Issues, and MAR Operations.

1.2 Water Research Foundation Project 5051

The Water Research Foundation (WRF) solicited bids from qualified research groups and consultants in November 2019. After a thorough review of proposal packages WRF awarded Project #5051 to Jacobs in December 2019, who subsequently began working on the project in September 2020. Project execution involved several interim milestones including preparing a project abstract, compiling literature describing research conducted on the geochemical aspects of MAR operations, developing a utility survey, plus preparing draft report outlines, the draft report, and draft Decision Framework tool (DFT). WRF circulated the interim deliverables internally, to the project subcommittee, and to utility partners for review and critical comment. The reviews improved the quality of each deliverable and hopefully will benefit MAR facilities in navigating geochemical issues.

1.3 Utility Participation

A critical characteristic of the project has entailed enlisting utilities to support project development, including reviewing interim deliverables as described previously, along with obtaining case and anecdotal experience on geochemical issues during MAR operations.

Utilities that participated in the project now operate or plan on operating MAR facilities in the future. Jacobs teamed with the following utilities as partners in the project:

- OCWD
- Truckee Meadows Water Authority (TMWA)
- Tucson Water, Tucson, Arizona
- The Water Corporation of Western Australia (WC), Perth, Australia
- Water Replenishment District of Southern California (WRD)

Physical and geochemical challenges experienced by personnel investigating and operating MAR facilities provide the most useful information for characterizing problems and developing potential solutions. Accordingly, a critical task during the project entailed developing a questionnaire that posed questions about physical and geochemical issues to utility operators in California, the conterminous United States and Australia. In addition to the above utilities partnering on the project, other utilities who completed the survey included:

- Anne Arundel County (AACo), Maryland
- Carpinteria Valley Water District (CVWD)
- Hampton Roads Sanitation District (HRSD), Virginia
- Soquel Creek Water District (SCWD), Santa Cruz, California
- Valley Water, Campbell, California
- Zone 7 Water Agency/Tri-Valley Agencies, Livermore-Amador Valley, California

In completing the surveys (Appendix B), utilities provided information on their recharge methods, receiving aquifers, facility capacities, water quality, geochemical issues and the benefit(s) each utility realized from embarking on operating or planning a MAR facility.

1.4 Project Framework

As stipulated by WRF, the project organization involved a simple framework designed to benefit utilities in operating MAR facilities and included the following tasks:

1. **Task 1: Literature Review:** Identify publications in the technical and scientific literature that describe physical and geochemical issues at MAR facilities and how utilities or researchers addressed the challenges.
2. **Task 2: Survey Utilities that Operate MAR facilities:** Worked with WRF's utility partners, locally and nationwide, to determine physical and geochemical issues most relevant to MAR facilities and how these issues are handled.
3. **Task 3: Framework Development:** Developed Excel-based DFT that supports utilities in handling clogging and geochemical issues during their efforts in developing and operating MAR facilities.
4. **Task 4: Final Deliverables:** Prepared project deliverables in the form of annotated bibliography, summary of utility survey results, memoranda, and a final framework report.

1.5 Constraints on Project 5051

The project focuses on applying MAR for potable reuse. Thus, utilities recharge secondary or tertiary wastewater treated to a high degree of purity at an AWT. As defined, the project does not focus on MAR systems that recharge stormwater or reclaimed wastewater without AWT. In addition, the project avoids discussing the physical and geochemical issues characteristic of ASR facilities, although many issues overlap with MAR projects.

Although the project report names constituents preferred for comprehensive analyses of recharge water, groundwater, and migrating recharge, the report avoids expounding on sampling techniques or laboratory methods. The report mentions several techniques for evaluating analytical data, however, covering all these techniques exceeds the scope of this work. Similarly, the report does not serve as a manual for the development, execution, and interpretation of geochemical models and their output.

1.5.1 Geographic Focus

Although many California utilities operating or planning MAR facilities have participated in the project, the project team welcomed input from utilities across the United States and worldwide. Accordingly, utilities from Arizona, Nevada, Virginia, Maryland, and Perth, Australia completed the utility surveys and shared their experiences (Figure 1-1). Other MAR facilities operate in the United States and worldwide, but elected not to participate in the project or, because of unfamiliarity with the utility, the project team did not to contact the utility.

1.5.2 Regulatory Issues

The technical content for the project is intended to apply to a global audience, evaluating geochemical challenges across various geographic regions and aquifer types. The regulatory framework for MAR can vary depending on the recharge source, mechanism for recharge, and federal and state regulations.

As an example, U.S. federal regulations such as the U.S. Environmental Protection Agency's (EPA) Underground Injection Control Program (UIC) established under the Safe Drinking Water Act, regulate recharge operations at MAR wells. However, many U.S. states, such as California, assume the primary regulatory role for the UIC program within the state borders. In addition, California has two different permitting frameworks for recharge via injection wells. When recharging treated wastewater, the facility is permitted under the indirect potable reuse regulations outlined in the Title 22 of the California Code of Regulations, and the State Water Resources Control Board (SWRCB) Water Quality Control for Recycled Water (SWRCB 2019). Recharge consisting of treated surface water is regulated under the Statewide Aquifer Storage and Recovery General Order (SWRCB 2012), and other recharge water types not fitting either of the aforementioned categories may require a site-specific permit. In addition, California has other regulations, such as SWRCB No. 68-16 regarding antidegradation that need consideration when implementing MAR under some circumstances (SWRCB 1968).

Other than published groundwater quality standards, regulations rarely involve rules explicit to geochemical issues. Therefore, due to the state-specific nature of regulating MAR projects, a comprehensive review of all regulatory considerations falls outside the scope of this project.

1.5.3 Intention of Project 5051 Report

This report seeks to incorporate all aspects of the project into a single document. Accordingly, the report includes elements of the literature search, utility surveys, and Decision Framework as chapters in the report. Moreover, WRF employed the report to obtain review comments on the flowcharts making up the DFT and thus, refining the tool before its publication.

1.6 Project Objectives

The project team based the implementation of the project on the following objectives:

1. Determine the influence of geochemical reactions on regulated and unregulated contaminants
2. Identify important recharge water parameters involved in reactions
3. Develop criteria for optimizing recharge water quality
4. Characterize and develop methods to minimize TSS loading
5. Guide utilities in:
    a. Aquifer selection
    b. Assessing geochemical compatibility
    c. Pretreatment techniques for recharge
    d. Long-term monitoring techniques

1.7 Report Organization

This report includes the following sections, followed by appendixes:

- Chapter 1—Introduction
- Chapter 2—Literature Review
- Chapter 3—Utility Survey
- Chapter 4—Framework Development
- Chapter 5—Conclusions and Recommendations
- Appendix A—Literature Review Summary
- Appendix B—Utility Survey Methodology
- Appendix C—Testing the Decision Framework using Utility Survey Responses
- References

Case studies form an important component of the report. The project team employed case studies in developing and refining the Decision Framework. The case studies originate with the utilities participating in the surveys.

CHAPTER 2

Literature Review

2.1 Objectives

The first task for the project involved conducting a comprehensive literature review. The intent of the literature review was to identify publications in the technical and scientific literature that describe physical and geochemical issues at MAR facilities, and how utilities addressed these challenges to provide a linkage between the body of literature and the decision support framework.

In developing the literature review, the project team constrained the search to how the topics listed in Section 2.2 relate to potable reuse MAR applications. An enormous number of publications deal with similar topics, but only distantly correspond to MAR applications and thus fall outside the scope of the review. However, the developers of this review included select, classic publications that may enrich the utility of the publications list. As an example, several publications feature testing or operational results from ASR facilities, a related but not equivalent technology to MAR. The main objective was to provide a comprehensive literature review that encompasses the various issued experienced during MAR, differing water quality parameters, and aquifer properties.

The literature review was thorough, current, and ongoing throughout this research project. This review emphasized issues requiring ongoing research, developing technology, and new approaches to addressing geochemical issues in situ. Results of the research strengthen the applicability of the decision support framework described in Chapter 4.

2.2 Methods

For the literature review, the project team compiled various sources devoted to geochemical issues experienced during MAR. The list of sources includes published papers, textbooks, proceedings, conference presentations, studies, articles etc. The literature summary is organized by major topic and subtopics and summarized in Table 2-1 (located at the end of this report).

An annotated bibliography, found in Appendix A, is organized alphabetically by topic, contains the citation, and includes a high-level abstract for each literature source. Table 2-1 provides a comprehensive list of the main topics relevant to MAR, sources, and the associated keywords that reference topics specific to the literature.

CHAPTER 3

Utility Survey

3.1 Survey Overview

The second task for the project involved creating and soliciting an extensive utility survey. The primary objective of the survey was to obtain important information relevant to MAR facilities and to gain a deeper understanding for the types of challenges faced and the solutions utilities have developed to overcome these issues. Appendix B contains information on the approach and methodology used in the utility survey.

3.2 Utilities Responding to Surveys

Twelve utilities responded the project survey, reporting on seven operating MAR facilities and seven facilities in various stages of planning (Table 3-1 Summary table). Three participants including the WC in Australia, WRD in Los Angeles County, California, and TMWA in Reno, Nevada, operate MAR facilities and have plans for developing separate facilities, or significantly expanding existing facilities using different technologies, like adding wells to a facility that relies on basins. The HRSD in Virginia operates a 1.0 million gallon per day (MGD) research facility while planning to develop MAR at four different locations, with a capacity exceeding 100 MGD.

Table 3-1. Summary of Utility Survey Results.

					Issues	
Utility	**Location**	**Phase of Operation**	**Capacity (MGD)**	**Recharge Facilities**	**Clogging**	**Geochemical Reactions**
WC	Perth, Australia	Operating	7.4	Wells	None noted	Cobalt and nickel appeared in samples collected from monitoring well in Yarragadee Aquifer
WC	Munster, Australia	Planning	12.7	Wells	Not applicable, yet	Not applicable, yet
Tri-Valley Agencies	Livermore-Amador Valley, California	Planning	5 to 12	Basins & Wells	Not applicable, yet	Not applicable, yet
HRSD	Virginia Beach, Virginia	Operating Research Facility	1	Wells	Yes	Conditioning to stabilize clays; Arsenic in monitoring wells at several discrete depths

					Issues	
Utility	**Location**	**Phase of Operation**	**Capacity (MGD)**	**Recharge Facilities**	**Clogging**	**Geochemical Reactions**
AACo	Annapolis, Maryland	Planning	8	Well	Not applicable, yet	Not applicable, yet
SCWD	Santa Cruz, California	Planning	1.3	Wells	Not applicable, yet	Not applicable, yet
Valley Water	Campbell, California	Planning	30	Basins	Not applicable, yet	Not applicable, yet
CVWD	Carpinteria, California	Planning	1	Wells	Not applicable, yet	Not applicable, yet
OCWD	Fountain Valley, California	Operating	>100	Basins & Wells	Clogging	Arsenic detected in monitoring well. Occasional NDMA detections in recharge water
TMWA	Reno, Nevada	Operating	Up to 8	Wells	Clogging	TTHM detected in monitoring well
TMWA	Reno, Nevada	Planning	2	Wells	Not applicable, yet	Not applicable, yet
Tucson Water	Tucson, Arizona	Operating	134	Basins	Clogging	None noted
WRD	Pico Rivera, California	Operating	100	Basins	Clogging	None noted
WRD	Long Beach, California	Operating/Planned Expansion	2 to 8	Wells	Clogging	None noted

Notes:
AACo = Anne Arundel County
NDMA = N-Nitrosodimethylamine
OCWD = Orange County Water District
TWMA = Truckee Meadows Water Authority
WC = Water Corporation of Western Australia
WRD = Water Replenishment District of Southern California

This chapter briefly describes each operating MAR facility and those in planning. Sections describe facility capacities, type of recharge facility (basin/wells), aquifer lithologies, the geochemistry of recharge, groundwater, and if appropriate, migrating recharge. Sections also discuss operational issues related to clogging and problems utilities have faced involving geochemical reactions. Information provided in this chapter relies on the thoroughness and care taken by utilities in completing the surveys.

3.2.1 Operating Utilities

3.2.1.1 Water Corporation’s Beenyup Groundwater Replenishment Scheme

WC of Western Australia, Perth, Australia, operates the Beenyup Groundwater Replenishment Scheme (Figure 3-1) along with planning a similar system located at the Perth southern suburb of Munster, Western Australia, with water sourced from the Woodman Point wastewater treatment plant described below. The survey completed by the utilities scientists indicates that WC operates eight MAR wells with recharge capacity up to a total approaching 23.8 MGD per year upon commissioning Stage 2 upgrades. At present WC recharges around 12 MGD. WC operates MAR wells in the Cretaceous-Age, Leederville and Jurassic-Age, Yarragadee Aquifers that range in depth from 400 to 4,300 feet below grade (fbg), respectively. Both aquifers consist of quartz sandstone exhibiting transmissivities ranging between 3,000 to 6,600 square feet per day (ft^2/d) for the Yarragadee and Leederville aquifers, respectively. Wells installed in the Yarragadee and Leederville aquifers recharge up to 3.3 and 3.9 MGD, respectively.

The project team selected the Beenyup Groundwater Replenishment Scheme as a case study applied to the DFT developed for this study. A discussion of the exercise appears in Appendix C.

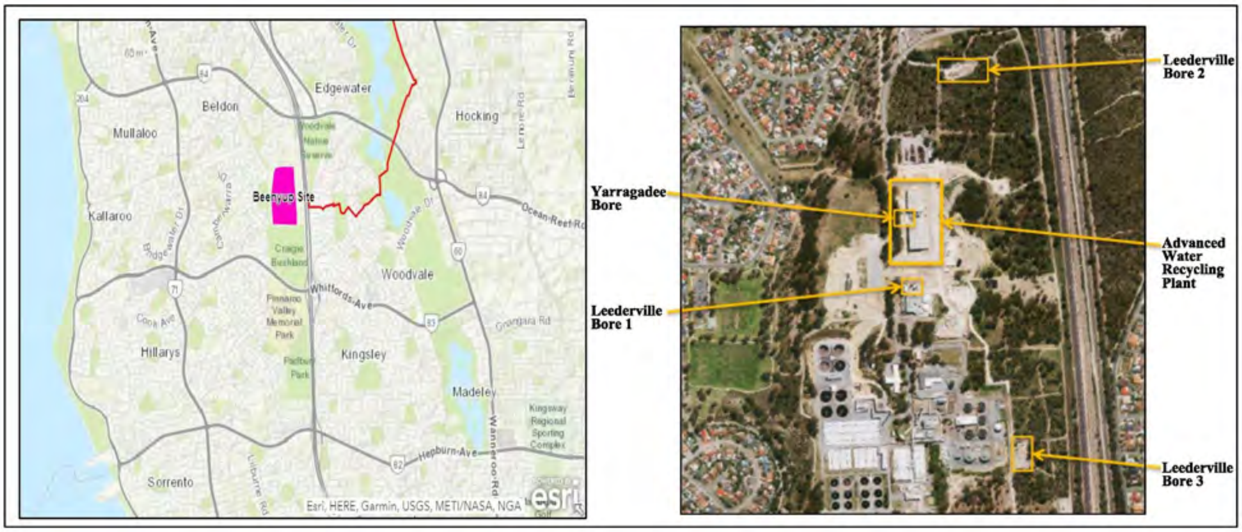


Figure 3-1. Water Corporation's Beenyup Groundwater Replenishment Scheme.

Recharge, Groundwater, and Migrating Recharge Chemistries

Entries on the utility survey supported describing the recharge, groundwater and migrating recharge chemistry at the Beenyup Groundwater Replenishment Scheme. Samples collected at monitoring wells located up to 150 feet from MAR wells operated by the WC, exhibited concentrations of nickel, but they did not exceed the Australian Drinking Water Guideline (ADWG) of 0.02 mg/L. Cobalt appeared in samples collected from the Yarragadee Aquifer at concentrations exceeding the ADWG of 0.001 mg/L. Reactive transport modeling results suggest that probably will not exceed the ADWG at the boundary of the Recharge Management Zone located 800 feet away from each MAR well.

Recharge Water Chemistry

WC’s AWT treats recharge using ultrafiltration (UF) and reverse osmosis (RO), degassing for stabilization, ultraviolet (UV) disinfection and monochloramine to manage biofouling in the MAR wells. The recharge chemistry (Table 3-2) reflects the treatment processes in the AWT, producing a dilute, circumneutral (pH 7.2), sodium chloride water as depicted on the Piper diagram shown on Figure 3-2.

Piper diagrams depict the major cations and anions in a water sample allowing comparison between large data sets (Mohammed and Garba Abba 2015). Chemistry plotting in the apices of the triangular elements on the lower left and right of the diagram represent major ions, while those plotting in the middle show a mixed chemistry with no major ions. Piper diagrams appear in each subsection discussing the recharge and groundwater chemistry of the project's utility partners.

Customization of the Piper diagrams for this report provide circles of varying diameters exemplifying relative total dissolved solids (TDS) concentrations for each sample. TDS concentrations are less than 25 mg/L (ionic strength 6.0×10^{-4} m/L) with sodium, alkalinity, and chloride representing the main ions, that display individual concentrations below 10 mg/L.

Table 3-2. Summary of Water Quality at WC Beenyup MAR Facility.

			Groundwater		**Migrating Recharge**	
Constituent	**Units**	**Recharge**	**Leederville**	**Yarragadee**	**Leederville**	**Yarragadee**
pH	Standard units	7.22	7.25	8	7.2	6.8
Dissolved oxygen	mg/L	8	<1	<1	<1	<1
TDS	mg/L	24	510	191	58	47
Calcium	mg/L	0.05[a]	30	10	2	2
Magnesium	mg/L	0.05[a]	13	5	2	1
Sodium	mg/L	8.1	120	54	13	13
Chloride	mg/L	6	250	38	9	8
Sulfate	mg/L	0.05[a]	17	1	12	13
Alkalinity	mg/L	9	59	129	18	4
Iron	mg/L	<0.01	6	0.04	1.5	0.1
Manganese	mg/L	<0.001	0.063	0.006	0.03	0.01
Arsenic	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001

[a] Concentration = half method detection limit

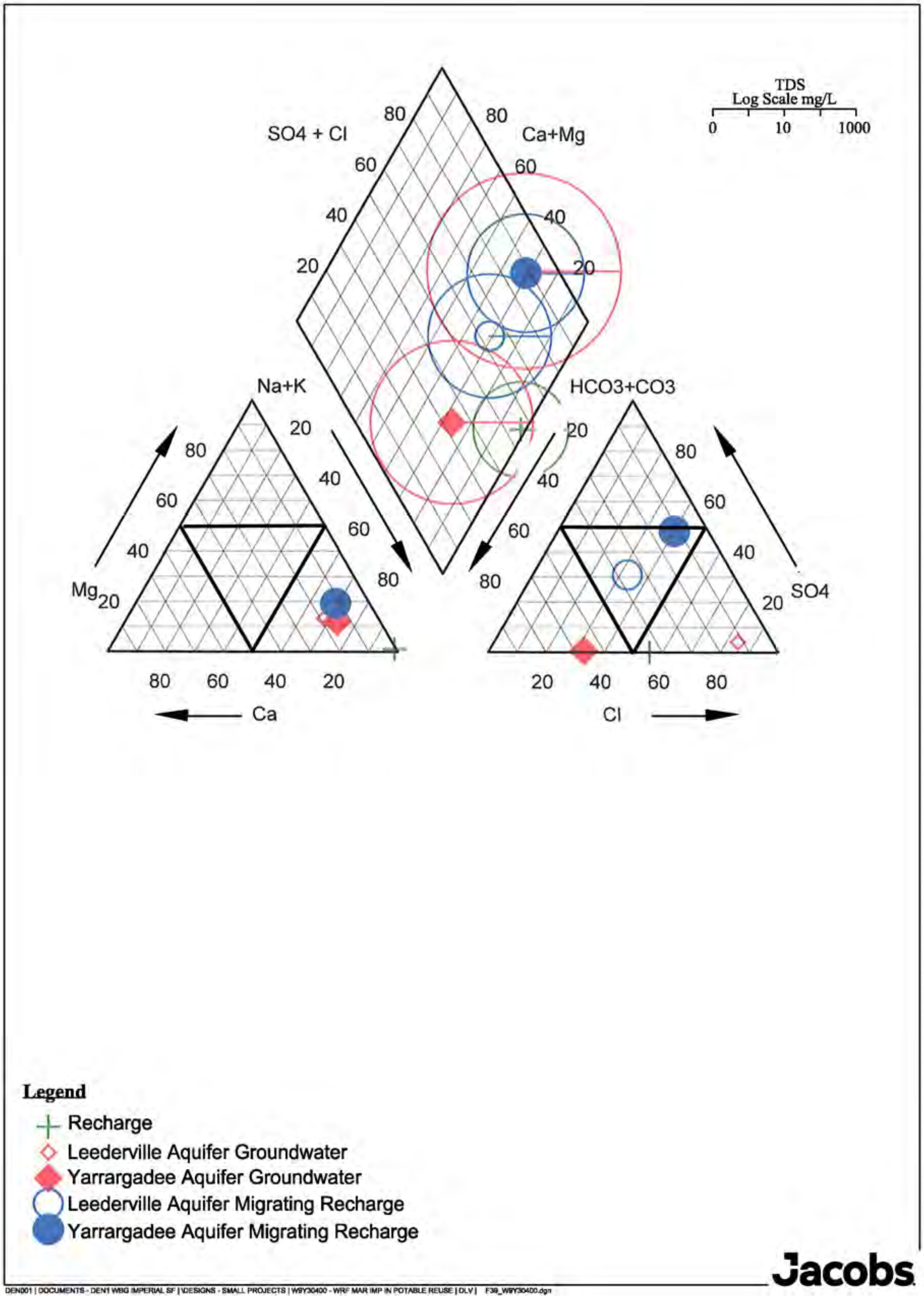


Figure 3-2. Piper Diagram Showing Iconic Composition of Recharge, Groundwater and Migrating Recharge at Water Corporation Beenyup’s Groundwater Replenishment Scheme.

Ionic strength and chemistry represent important considerations for MAR facilities. Ionic strength, reported in m/L is a function of all ions present in a solution, measuring the concentration of all ions scaled for each type of ion by its charge. The parameter becomes important when the ionic strength of the groundwater exceeds the recharge by over an order of magnitude. Introducing a low ionic-strength recharge water into an aquifer displaces groundwater containing positive charges away from negatively charged clay mineral surfaces creating a repulsive environment. Clay minerals disperse, swell, fragment, and migrate with the groundwater flow.

Dispersing clays represent a special type of formation damage (Civan 2000). Migrating clays can accumulate in pore throats (brush pile), clogging the flowpath and reducing aquifer permeability. Formation damage occurs rapidly, severely lowers permeability, and usually proves irreversible when applying conventional rehabilitation methods to basins or wells. Less commonly, the ionic strength of groundwater can fall below that of the recharge water. The relationship becomes a concern if a single prevailing cation in the recharge exhibits greater concentrations than the others. An as example, elevated sodium in recharge can cause formation damage in a clastic aquifer containing low ionic-strength groundwater.

Common cations, including calcium, potassium, magnesium, and sodium, in recharge water can influence how recharge reacts with clay minerals occupying the interstices of sands or sandstone aquifers. Exchanging cations between the recharge water and interstitial clays can create another type of formation damage if the reactions damage the clay mineral edge, cause it to fragment, migrate, and eventually brush pile in pore throats. Differing dominant cations in the recharge and groundwater often indicate a potential for exchange reactions during MAR operations.

The survey did not contain an entry for DO concentrations in recharge. Considering the treatment processes, the report assumed DO concentrations were near the saturated limits for water at 10 mg/L. A computer program developed by the U.S. Geological Survey (USGS) that evaluates the common redox indices (DO, nitrate, manganese, iron, and sulfate) returned an oxic redox and oxygen reduction for the primary redox process(Jurgens, et al. 2009). Table 3-3 outlines the approach for evaluating redox species, while Table 3-4 present the resulting assigned primary redox category and redox process for each sample undergoing evaluation using the program.

Table 3-3. Criteria and Threshold Concentrations for Identifying Redox Processes in Ground Water.

Redox category	Redox process[a]	Electron acceptor (reduction) half-reaction [b]	Criteria for inferring process from water-quality data					
			Dissolved oxygen (mg/L)	Nitrate, as Nitrogen (mg/L)	Manganese (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Iron/sulfide (mass ratio)
Oxic	O2	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	≥0.5	—	<0.05	<0.1	—	
Suboxic	Suboxic	Low O2; additional data needed to define redox process	<0.5	<0.5	<0.05	<0.1	—	
Anoxic	NO3	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6\ H_2O$; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	<0.5	≥0.5	<0.05	<0.1	—	
Anoxic	Mn(IV)	$MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	<0.5	<0.5	≥0.05	<0.1	—	
Anoxic	Fe(III)/SO4	Fe(III) and (or) $SO4^{2-}$ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	no data
Anoxic	Fe(III)	$Fe(OH)_{3(s)} + H^+ + e^- \rightarrow Fe^{2+} + H_2O$; $FeOOH_{(s)} + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	>10
Mixed (anoxic)	Fe(III)-SO4	Fe(III) and $SO4^{2-}$ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	≥0.3, ≤10
Anoxic	SO4	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	<0.3
Anoxic	CH4gen	$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$	<0.5	<0.5	—	≥0.1	<0.5	

Table was modified from Jurgens et al. 2009

[a] Redox Process: O_2, oxygen reduction; NO_3, nitrate reduction; Mn(IV), manganese reduction; Fe(III), iron reduction; SO_4, sulfate reduction; CH4gen, methanogenesis

[b] Chemical species: O_2, dissolved oxygen; NO_{3-}, dissolved nitrate; MnO2(s), manganese oxide with manganese in 4+ oxidation state; Fe(OH)3(s), iron hydroxide with iron in 3+ oxidation state; FeOOH(s), iron oxyhydroxide with iron in 3+ oxidation state; SO42–, dissolved sulfate; CO2(g), carbon dioxide gas; CH4(g), methane gas

— criteria do not apply because redox processes do not influence the species concentration

Table 3-4. Summary of Redox Assignments for Sample Data from Utility Surveys.

	Redox Variables[a]	***O_2***	***NO_3^- (as N)***	***Mn^{2+}***	***Fe^{2+}***	***SO_4^{2-}***	***Sulfide (sum of H_2S, HS^-, S^{2-})***	***Redox Assignment***			***Fe^{2+}/ Sulfide, ratio***
	Units	**(mg/L)**	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(mg/L)**	**(mg/L)**				
Sample ID	**Threshold values**	**0.5**	**0.5**	**50**	**100**	**0.5**	**none**	**Num of Params**	**General Redox Category**	**Redox Process**[b]	
OCWD Recharge		6	0.7	1	5	0.5	0.06	6	Oxic	O2	
OCWD Talbert GW		0.34	0.01	19	208	0.3	0.05	6	Anoxic	CH4gen	
OCWD MBI GW		0.04	0.05	9	16	36	0.03	6	Suboxic	Suboxic	
OCWD Forebay GW		0.03	0.01	10	15	0.05	0.03	6	Suboxic	Suboxic	
OCWD Talbert MR		3	1.4	2	2	2.8	0.01	6	Oxic	O2	
OCWD MBI MR		3.2	1	1	6	3.9	0.005	6	Oxic	O2	
OCWD forebay MR		7	1	3	115	1.2	0.01	6	Mixed(oxic-anoxic)	O2-Fe(III)	11.50
Tucson Recharge		8	0.01	10	21	219	0.01	6	Oxic	O2	
Tucson GW		0.01	1.6	10	10	9	0.01	6	Anoxic	NO3	
Tucson MR		0.01	2.4	2	10	184	0.01	6	Anoxic	NO3	
AACo Recharge		8	0.8	12	5	35	0.01	6	Oxic	O2	
AACo GW Upper PAS		0.01	0.8	40	3000	5	0.01	6	Mixed(anoxic)	NO3-Fe(III)	300.00
AACo GW Lower PAS		0.01	0.8	100	3000	16	0.01	6	Mixed(anoxic)	NO3-Fe(III)	300.00
HRSD Recharge		15	3.5	100	50	63	0.01	6	Mixed(oxic-anoxic)	O2-Mn(IV)	
HRSD PAS GW		0.01	0.1	12	2400	151	0.01	6	Anoxic	Fe(III)	240.00
HRSD MR		0.01	0.5	10	20	86	0.01	6	Anoxic	NO3	
Valley Water Recharge		8.7	2.2	10	10	0.3	0.01	6	Oxic	O2	
Valley Water GW		0.01	0.1	13000	22000	44	0.01	6	Anoxic	Fe(III)	2200.00
WC Beenyup Recharge		8	1.3	0.5	5	0.05	0.01	6	Oxic	O2	
WC Beenyup LV GW		0.01	0.005	6	40	1.1	0.01	6	Anoxic	Fe(III)	
WC Beenyup LV MR		0.01	0.07	30	1500	11.8	0.01	6	Anoxic	Fe(III)	
WC Beenyup YG GW		0.01	0.005	6	40	1.1	0.01	6	Suboxic	Suboxic	
WC Beenyup YG MR		0.01	0.04	12	100	13.1	0.01	6	Mixed(anoxic)	Fe(III)-SO4	
WC Wm Pt Recharge		10	14	19	31	47	0.01	6	Oxic	O2	
WC Wm Pt LV GW		0.01	0.025	30	2100	82	0.01	6	Anoxic	Fe(III)	210.00
WC Wm Pt YG GW		0.01	0.025	30	250	80	0.01	6	Anoxic	Fe(III)	25.00

[a] Redox variables: O_2, dissolved oxygen; NO_{3-} (as N), dissolved nitrate; Mn2+, manganese ion; Fe2+, ferrous iron; SO42–, sulfate

[b] Redox Process: O_2, oxygen reduction; NO_3, nitrate reduction; Mn(IV), manganese reduction; Fe(III), iron reduction; SO_4, sulfate reduction; CH4gen, methanogenesis

GW = Groundwater
LV = Leederville Aquifer
MBI = Mid-Basin Injection
MR = Migrating Recharge
OCWD = Orange County Water District
PAS = Potomac Aquifer System
TWMA = Truckee Meadows Water Authority
WC = Water Corporation
Wm Pt = Woodman Point
YG = Yarragadee Aquifer

Groundwater Chemistry

The following section describe the groundwater chemistry in the Leederville and Yarragadee Aquifers, respectively.

3.2.1.2 Leederville Aquifer

Groundwater samples from the Leederville Aquifer displayed a fresh water (TDS less than 1,000 mg/L; Hem 1985) with a circumneutral pH and sodium—chloride chemistry. Iron concentrations at around 1.5 mg/L significantly exceeded ADWGs of 0.3 mg/L while manganese concentrations were below the standard of 0.05 mg/L at 0.03 mg/L. Arsenic concentrations in groundwater from the Leederville Aquifer were below laboratory method detection limits (MDL). Evaluation of redox species produced anoxic and iron-reducing conditions for the redox category and redox process, respectively (Table 3-4). The modestly elevated sulfate concentrations suggest that pyrite oxidation may occur in the Leederville Aquifer.

3.2.1.3 Yarragadee Aquifer

Groundwater from the Yarragadee Aquifer exhibited a fresh, mildly alkaline, sodium bicarbonate chemistry. Despite its greater depth, TDS concentrations in the Yarragadee Aquifer were below those found in samples from the Leederville Aquifer, suggesting differing sources of recharge and likely minimal vertically downward recharge through Leederville Aquifer. Iron, manganese, and arsenic concentrations fluctuated around their respective MDLs and did not exceed ADWGs. Sulfate concentrations equaled around 1 mg/L suggesting pyrite oxidation does not naturally occur in the Yarragadee Aquifer

Migrating Recharge

The quality of migrating recharge samples from both the Leederville and Yarragadee Aquifers suggests migrating recharge had passed the respective monitoring wells prior to collecting the samples containing cobalt and nickel (Yarragadee Aquifer only). Both sets of samples showed chemistry that differed significantly from the historical groundwater from each aquifer.

Recharge water migrating in the Leederville Aquifer displayed a chemistry controlled by reactions with aquifer minerals. In comparing the recharge and migrating recharge chemistries, the differences comprised diminished nitrate, with increased concentrations of iron, manganese, sulfate and alkalinity (Figure 3-3). The pH of the migrating recharge remained equivalent to recharge prior to entering the Leederville Aquifer. The highly elevated iron, manganese, sulfate and alkalinity infers that recharge reacted with the iron carbonate mineral, siderite ($FeCO_3$) along with pyrite (FeS_2), the most common sulfide mineral (Evangelou 1995). WC analysis also identified fluorapatite and feldspar dissolution as geochemically active during MAR operations. Water-rock reactions produced a more buffered migrating recharge that maintained a stable pH, but still elevated sulfate concentrations. Migrating recharge in the Leederville Aquifer displayed a sodium—mixed anion chemistry compared to the sodium chloride chemistry displayed by recharge.

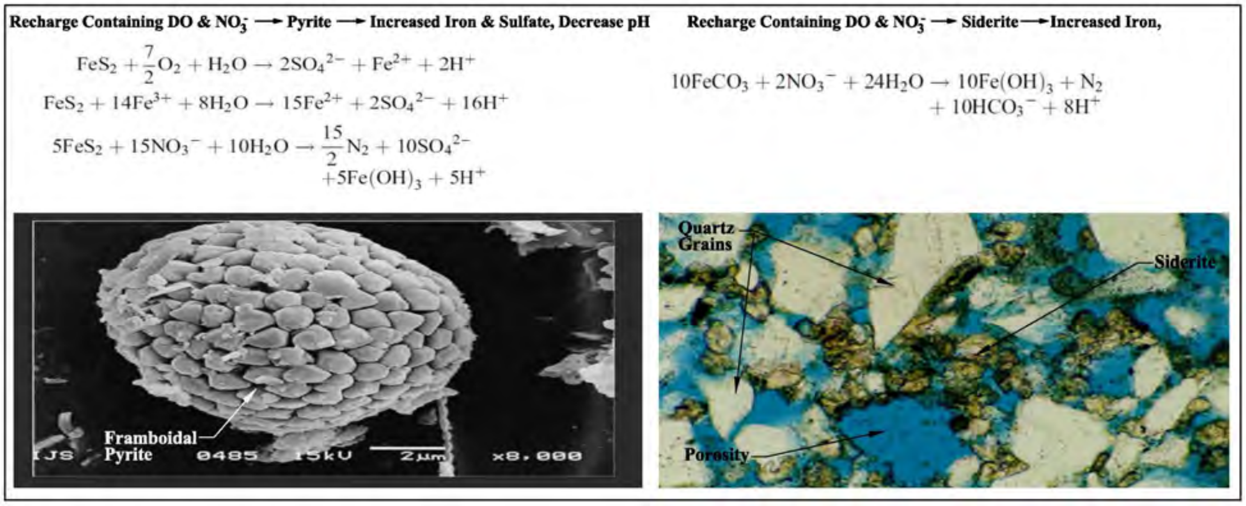


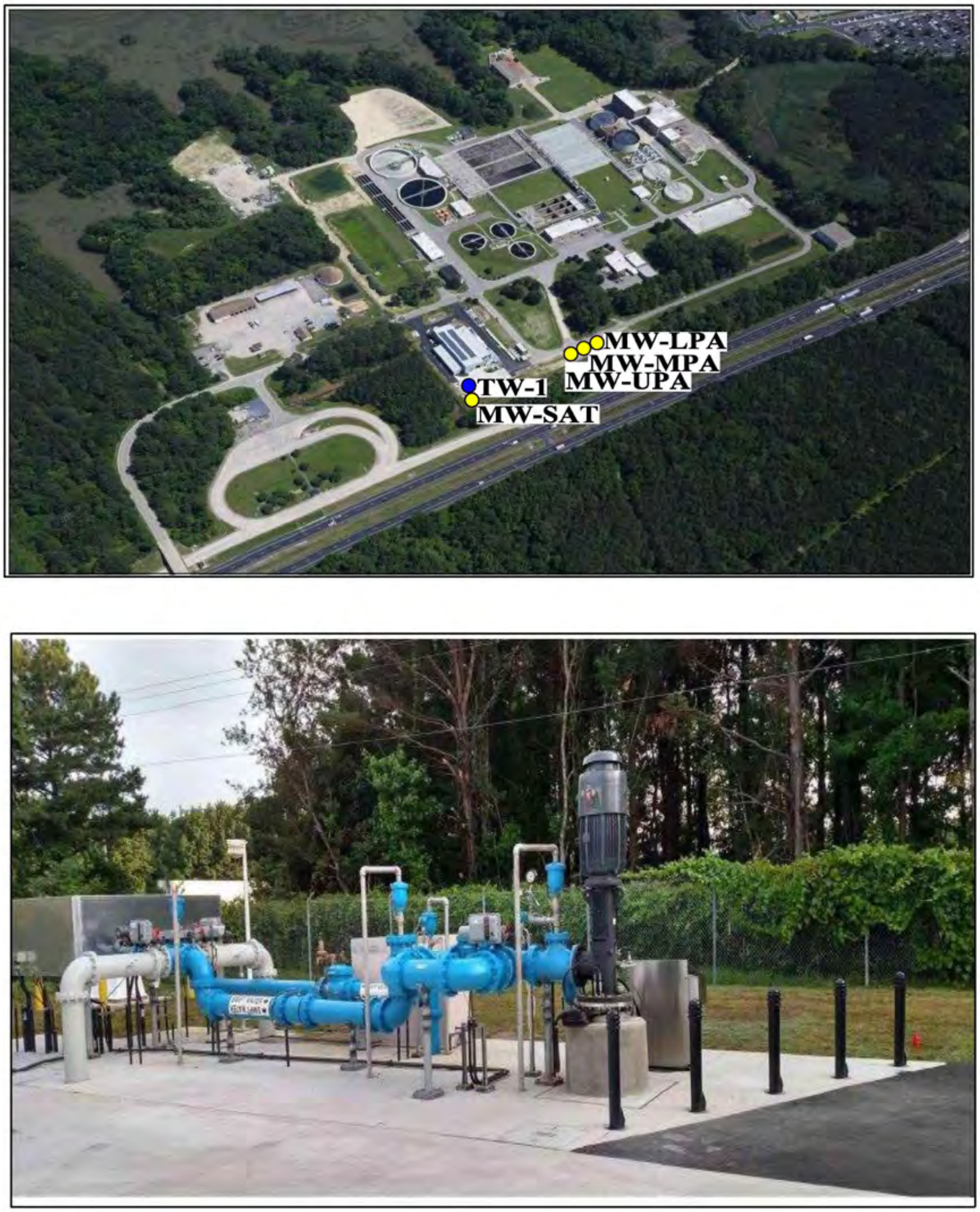
Figure 3-3. Pyrite and Siderite Dissolution during MAR Operations.

In addition to cobalt and nickel, groundwater samples from the Yarragadee Aquifer displayed other prominent geochemical indices including reduced pH, nitrate and alkalinity, plus increased concentrations of iron, manganese, and sulfate. Sulfate concentrations proved elevated enough to change the ionic composition from a sodium bicarbonate in the recharge to a sodium-mixed anion-sulfate (Figure 3-2) chemistry in the migrating recharge. Thus, migrating recharge from the Yarragadee Aquifer exhibited evidence of the abiotic oxidation of FeS_2. Declining nitrate concentrations suggests, that in addition to DO, nitrate may have served as an electron acceptor during the oxidation of pyrite

Arsenic concentrations greater than the MDL did not appear in migrating recharge in samples from the Leederville or Yarragadee Aquifer. Moreover, even though migrating chemistry from both aquifers showed evidence of pyrite oxidation, nickel and cobalt emerged only in samples from the Yarragadee Aquifer, indicating that the pyrite composition between the two units likely differs.

3.2.1.4 Hampton Roads Sanitation District Sustainable Water for Tomorrow Research Center

The HRSD Sustainable Water Initiative for Tomorrow (SWIFT) Research Center (SRC; Figure 3-4) consists of a 1 MGD AWT recharging water to a test well (TW-1) screened across the upper, middle, and lower zones of the Potomac Aquifer System (PAS) in Nansemond, Virginia. The PAS comprises a major aquifer system underlying the Atlantic Coastal Plain Physiographic Province. The Cretaceous-Age, unconsolidated sand aquifer extends beneath New Jersey, Delaware, Maryland, Virginia, and North Carolina. TW-1 screens nearly 400 feet of sand beneath SRC, however, individual screens range in length from 15 to 105 feet, with most falling below 40 feet in length.



Legend

TW-1: MAR Test Well
MW-SAT: Depth Discrete FLUTe Monitoring Well
MW-UPA: Monitoring Well in Upper Potomac Aquifer
MW-MPA: Monitoring Well in Middle Potomac Aquifer
MW-LPA: Monitoring Well in Lower Potomac Aquifer

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Figure 3-4. HRSD Test Well TW-1 Plus Wellhead.

The SRC AWT treats secondary wastewater using flocculation/sedimentation (floc/sed), ozone oxidation, biologically activated carbon (BAC) filtration, granular activated carbon (GAC) adsorption, UV disinfection followed by sodium hypochlorite addition before recharging the effluent to TW-1 (Figure 3-5). A downhole control valve (DHCV) installed in the pump column prevents entraining air during recharge. HRSD has invested significant funds installing monitoring wells and sampling at SRC including a depth discrete sampling well (MW-SAT) containing eleven sampling ports (Figure 3-6), each representing individual sand units in the PAS, and screens (Screens 1 through 11) in MW-SAT and TW-1. Situated 50 feet away from TW-1, MW-SAT forms a portion of a network including conventional monitoring wells that fully penetrate the upper, middle and lower aquifer zones, located 250 to 350 feet away. Sampling up to four times daily accommodated tracking the front of recharge migrating through each of the eleven sand units monitored in MW-SAT.

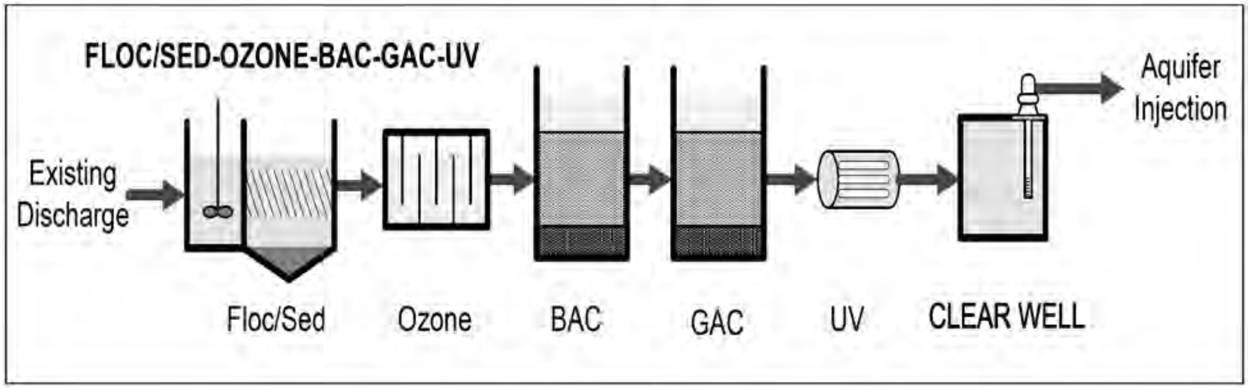
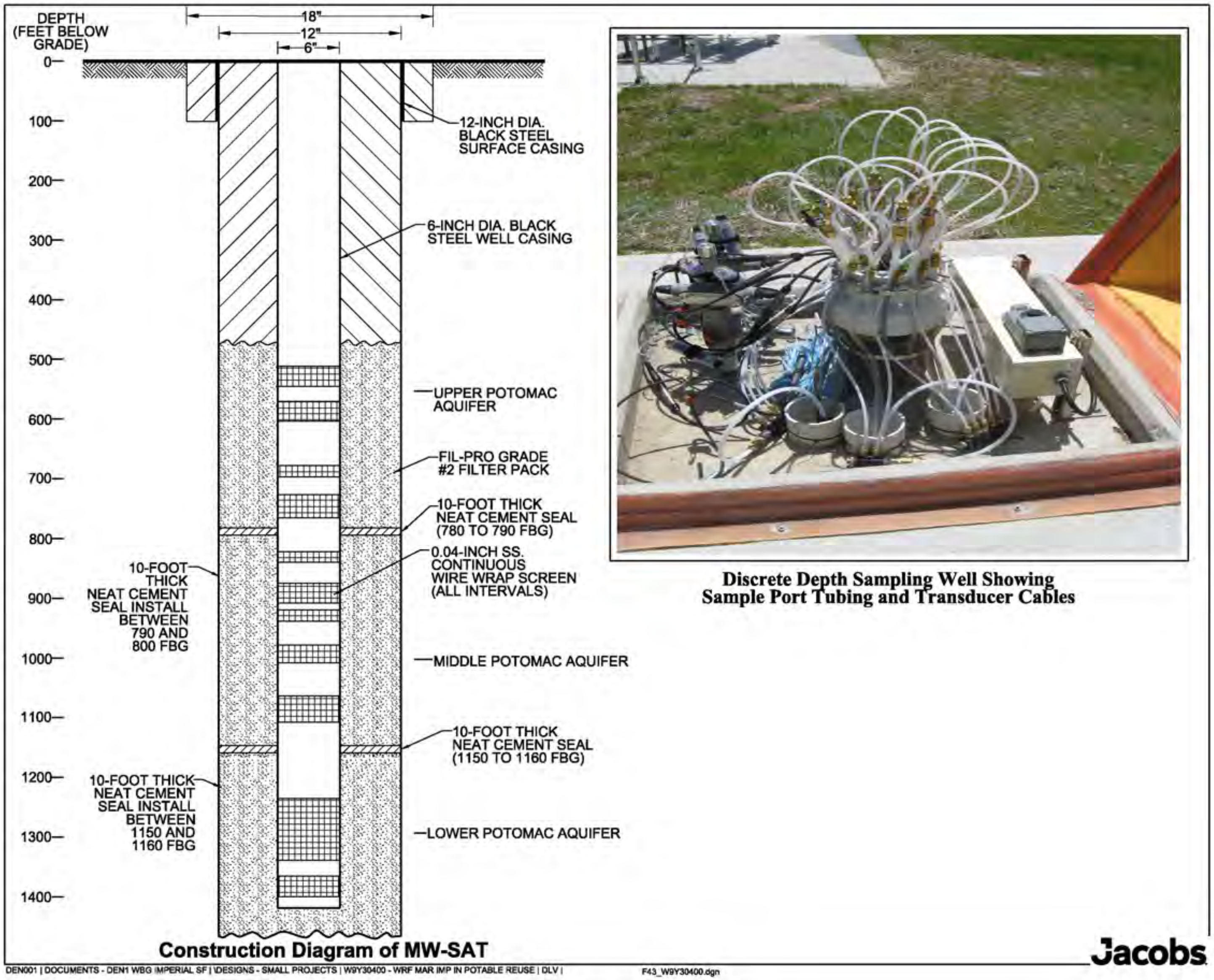


Figure 3-5. Schematic of Treatment Process at Hampton Roads Sanitation District's SWIFT Research Center.



Construction Diagram of MW-SAT

Discrete Depth Sampling Well Showing Sample Port Tubing and Transducer Cables

Figure 3-6. HRSD's MW-SAT Depth Discrete Sampling Monitoring Well.

Although a relatively small facility, because of the volume of data collected and evaluated by HRSD, SRC provides information for two the case studies appearing in Appendix C.

Recharge Chemistry

Recharge displays TDS concentrations around 660 mg/L, a pH adjusted to 7.6, DO concentrations exceeding 15 mg/L and a sodium—chloride chemistry (Table 3-5; Figure 3-7). HRSD increases the pH from 6.9 to above 7.6 with sodium hydroxide prior to recharge. In combination with the elevated DO, the pH helps passivate reactive metal-bearing minerals in situ by precipitating a hydrous ferric oxide (HFO) mineral coating on the mineral surface. The coating reduces the reactivity of the mineral surface along with serving as an adsorption surface for metals migrating in the aquifer environment.

Table 3-5. Summary of Water Quality at HRSD SRC MAR Facility.

			Groundwater	Migrating Recharge
Constituent	**Units**	**Recharge**	**PAS**	**PAS**
pH	standard units	7.6	7.2	8.1
Dissolved oxygen	mg/L	17	0.01	0.5
Calcium	mg/L	17	41	23
Magnesium	mg/L	5	19	1.9
Sodium	mg/L	190	1270	52
Chloride	mg/L	190	14	14
Sulfate	mg/L	63	1270	36
Alkalinity	mg/L	200	300	126
Iron	mg/L	0.01	2.4	0.01
Manganese	mg/L	0.02	0.12	0.1
Arsenic	mg/L	<0.001	0.001	0.0002

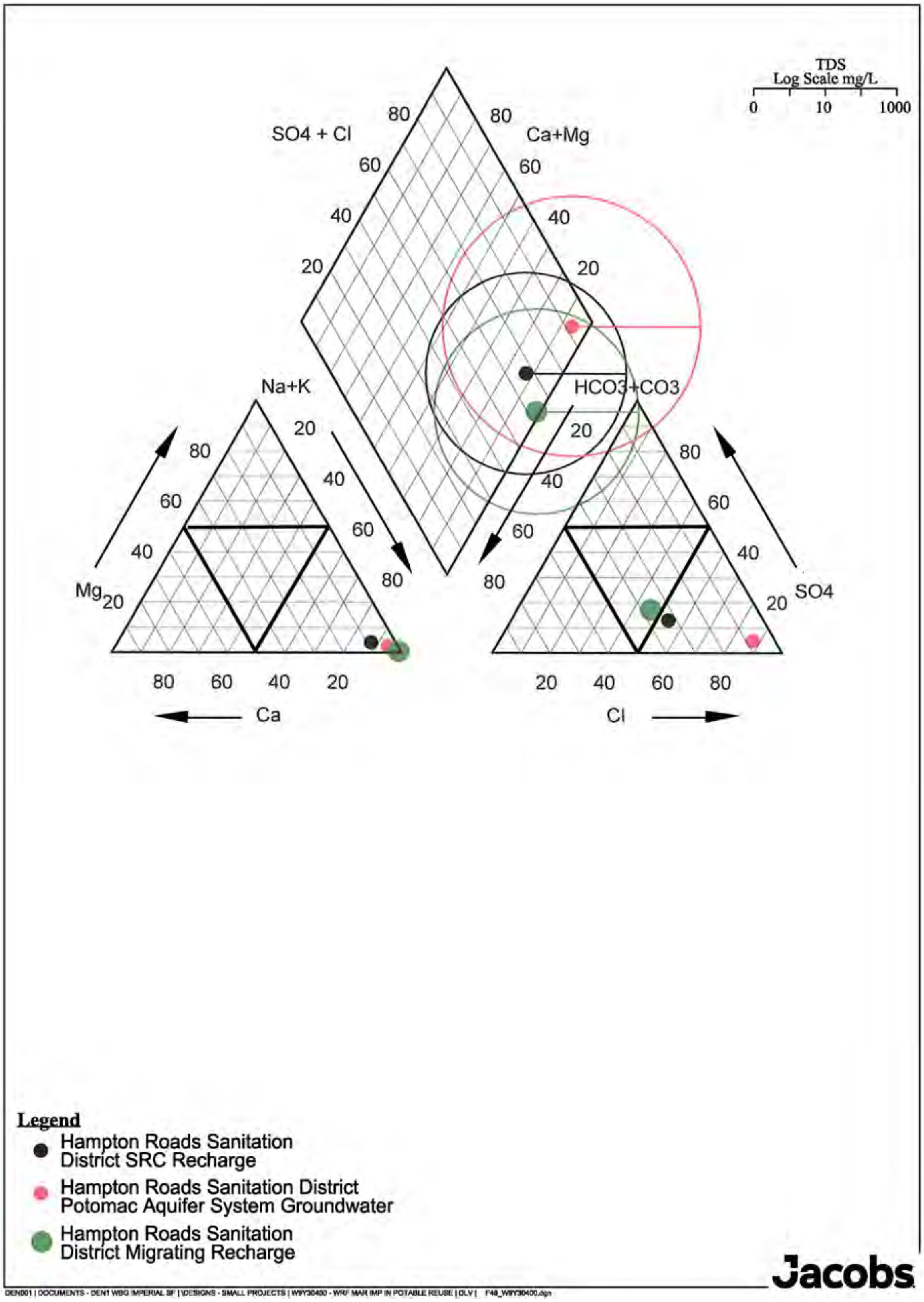


Figure 3-7. Piper Diagram Showing Ionic Composition of Recharge, Groundwater and Migrating Recharge for HRSD SRC.

HRSD conducts membrane filter index (MFI) testing frequently to track how adjusting treatment processes at SRC affect the particulate loading to the recharge. Recent literature advocates an MFI of less than 3 seconds per liter squared (sec/L^2) for trouble-free MAR operations. Unfortunately, MFIs at SRC average higher than 10 sec/L^2 with the higher than recommended index reflected in an elevated maintenance routine focused on controlling the injection specific capacity (injectivity) of TW-1. HRSD backflushes TW-1 every 12 hours and takes other measures to preclude loading particulates to the well.

Groundwater

With TW-1 screening 11 sands through the upper, middle, and lower PAS, groundwater chemistry varies significantly with depth. TDS, sodium, chloride, iron, and manganese concentrations increase with depth while the pH ranges between 7 and 7.5. Groundwater from all zones screened by TW-1 display a sodium chloride chemistry like the recharge. In addition, radionuclide activities progressively increase with depth in TW-1 with gross alpha and total radium exceeding 30 and 8 picocuries per liter (pCi/L) in the deepest screens. Radionuclides do not constitute a significant threat to MAR operations. Radium, a divalent ion, behaves like calcium traveling with groundwater as it migrates away from the MAR well or basin.

Samples from TW-1 exhibit brackish concentrations of TDS (TDS > 1,000 mg/L) even from the shallowest sand intervals but increase to greater than 5,000 mg/L in the deepest intervals. Consequently, the differences in ionic strength between the recharge and groundwater exceed one order of magnitude, a threshold prompting the need for treatment with divalent or trivalent salts like calcium or aluminum, respectively.

Recharging fresh water into an aquifer containing brackish or saline groundwater displaying an ionic strength differing by one order of magnitude (Gray and Rex 1966; Reed 1972) can reduce the charge environment around clay minerals initiating swelling and dispersion. Swelling and fragmenting clay minerals constrict pores, while migrating clays can brush pile (accumulate) in pore throats. Even at this microscopic level, formation damage in the form of permeability reduction develops rapidly, irreversibly reducing injectivity within hours of starting recharge. Accordingly, HRSD treats their test wells using aluminum-salts (Al-salts) before recharging fresh AWT effluent or potable water for testing. A treatment program involving Al-salts in the form of aluminum chlorohydrate (ACH) complimented with extensive hydraulic testing appears in Appendix C. To date, none of the five test wells installed by HRSD has experienced catastrophic specific capacity losses during recharge testing.

Migrating Recharge

With time, migrating recharge chemistry closely resembled AWT effluent produced at SRC. However, the chemistry varies at the front of migrating recharge water (Figure 3-8). Samples originating from ports in the depth discrete monitoring well showed evidence of pyrite oxidation including lowering concentrations of DO, nitrate, and alkalinity coinciding with elevating concentrations of iron and manganese (Figure 3-9). In addition, Screens 1, 2, and 4 displayed elevated concentrations of arsenic time coincident with pyrite oxidation, however arsenic concentrations did not exceed the PMCL of 10 micrograms per liter (µg/L). The pyrite oxidation signature disappeared in most zones over a period of several days.

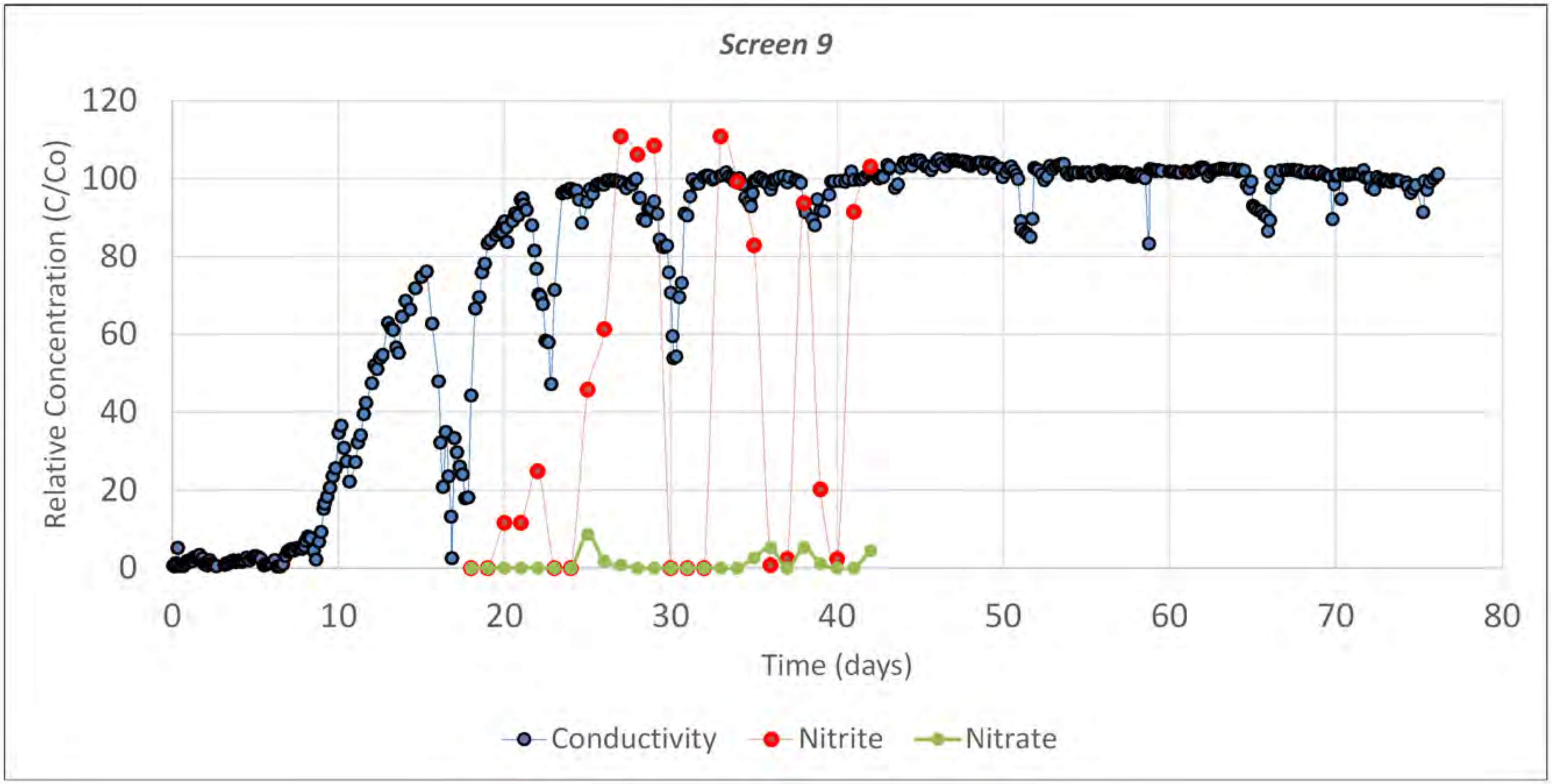


Figure 3-8. Breakthrough Curve in MW-SAT Screen 9 Using Specific Conductivity as Tracer.

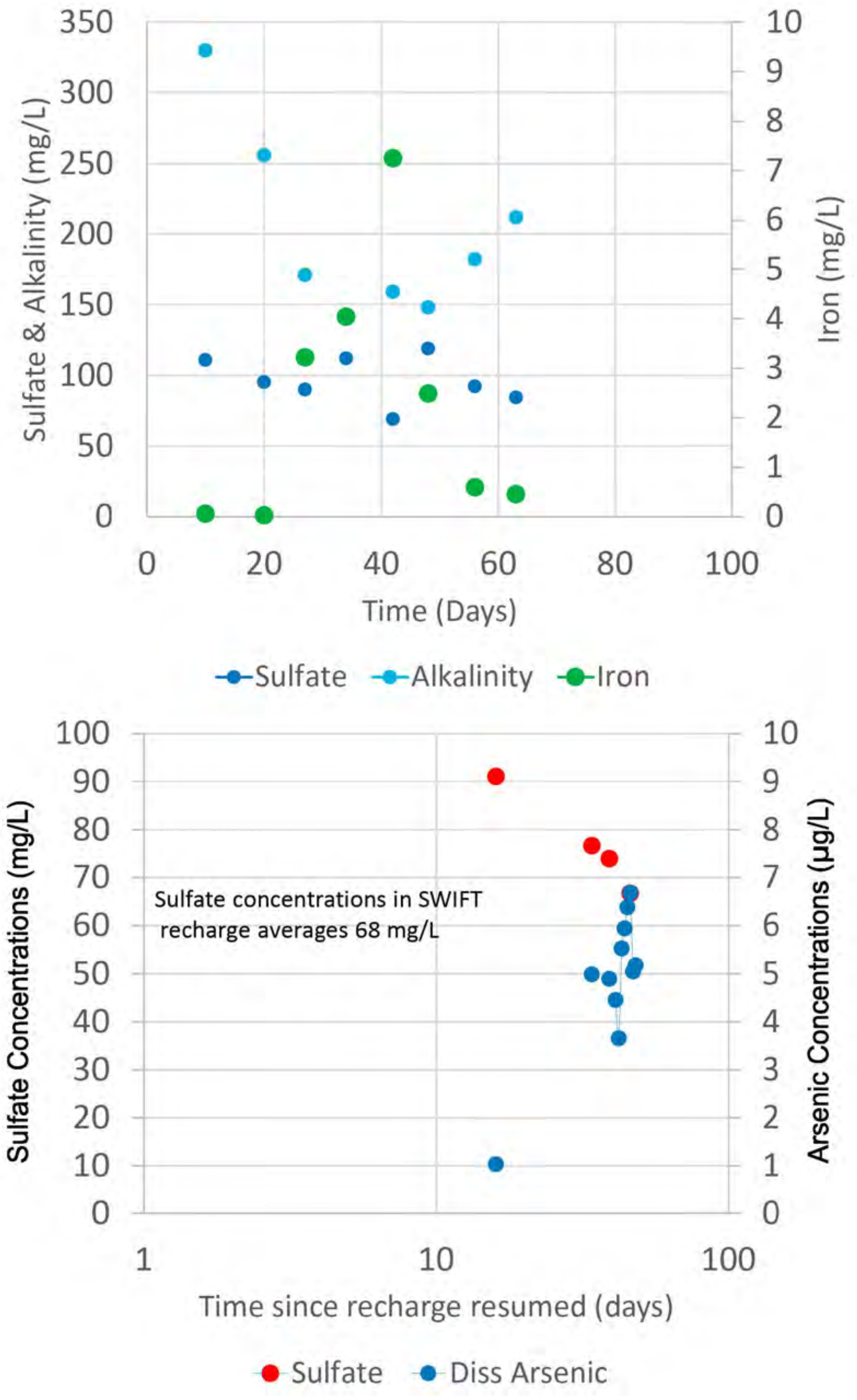


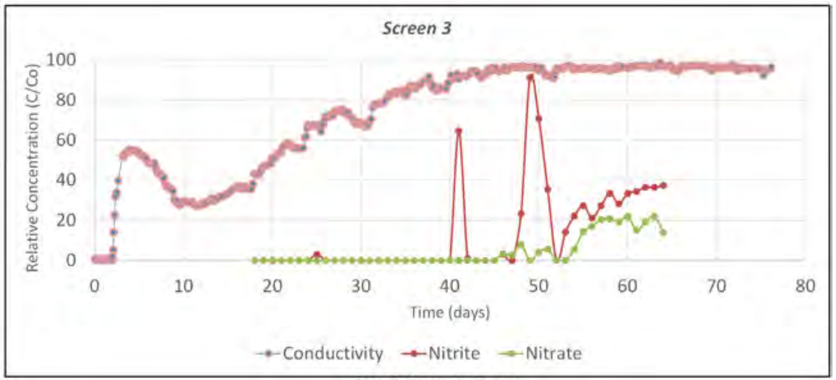
Figure 3-9. Evidence of Pyrite Oxidation and Arsenic Mobilization in Screen 9 at HRSD's MW-SAT.

In addition to pyrite oxidation, several zones displayed denitrification, with nitrate concentrations in the recharge progressively increasing in Screens 3 and 9, while producing nitrite concentrations approaching the PMCL of 1 mg/L (Figure 3-10). The reaction appeared slightly attenuated compared with the passing of the recharge front and may depend on the production of ferrous iron during pyrite oxidation. Thus, ferrous iron may serve as an electron donor in the reducing nitrate. Once the influence of pyrite oxidation dissipated, including ferrous iron production, nitrate concentration in the recharge broke through.

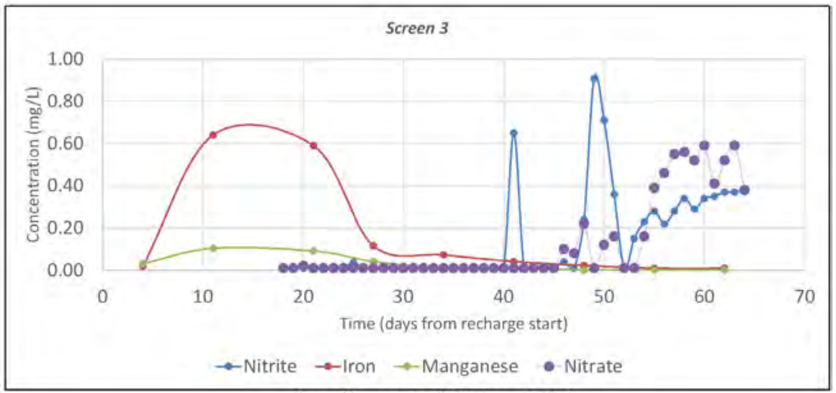
The volume of data collected at HRSD SRC support several topics of interest to this study including:

- Well clogging
- Conditioning clay minerals
- Recharge/ mineral reactions
    - Pyrite oxidation
    - Arsenic mobilization
- Denitrification

Appendix C discusses well clogging and conditioning clay minerals at HRSD's SRC in applying the DFT.



Breakthrough Curve



Iron, Manganese, Nitrate and Nitrite

Figure 3-10. Breakthrough in MW-SAT Screen 3 Compared with Ferrous Iron, Nitrate and Nitrite.

3.2.1.5 Orange County Water District

The OCWD’s Groundwater Replenishment System project represents one of the largest and oldest MAR system in the United States featuring the planned use of recycled water, dating from the late 1970s when its predecessor facility, Water Factor 21, went online. OCWD’s implements MAR activities in the Orange County Groundwater Basin. The basin includes multiple sectors dedicated for MAR activities, including the Forebay area, the Talbert Barrier, and the Mid-Basin Injection (MBI) area (Figure 3-11). OCWD has also separated several operational areas into sub-basins.

Through the Groundwater Replenishment System and other MAR activities, OCWD recharges over 150 MGD through 27 basins and over 100 MAR wells. The basins display capacities ranging from 0.6 to 60 MGD while wells recharge at rates ranging from 10 to 1,500 gallons per minute (gpm). More recently, OCWD has established a recharge target of 2 MGD for new MAR wells. Furthermore, OCWD has equipped only eight of the 107 wells with a dedicated pump suitable for backflushing, while using airlift pumping via a portable air compressor at the others.

Information provided by OCWD supported two of the case studies appearing in Appendix C. One case study discusses how OCWD maintains their MAR wells at peak performance while the second describes a unique mechanism for arsenic mobilization in the surficial aquifer beneath MAR basins. The second case study originally appeared in a refereed article published in Environmental Science and Technology (ES&T) in 2015 (Fakhreddine, et al. 2015). ES&T described non-redox related arsenic desorption from clay minerals after infiltrating high purity recharge into underlying unconfined unconsolidated alluvial aquifer (Figure 3-12) displaying oxic conditions at OCWD’s Miraloma Basin in the Forebay portion of the Orange County Groundwater Basin.

In addition to the two case studies, a second publication appearing in ES&T (Fakhreddine et al. 2020) described testing at a well that recharged three discrete intervals in a confined aquifer with the zones displaying heterogeneity and varying redox characteristics. The three zones exhibited varying degrees of oxidation attributed to historic, long-term infiltration into the shallow overlying aquifer. Samples collected from monitoring wells located 89 and 640 feet downgradient of the MAR well, in Fountain Valley and Santa Ana, California, respectively, helped define the geochemical characteristics of migrating recharge. Both the MAR Basin and injection well received recharge water that originated from the same AWT.

This section describes recharge chemistry, groundwater chemistry from the MAR sectors provided by OCWD in the utility surveys, and groundwater and migrating recharge from the two ES&T publications.

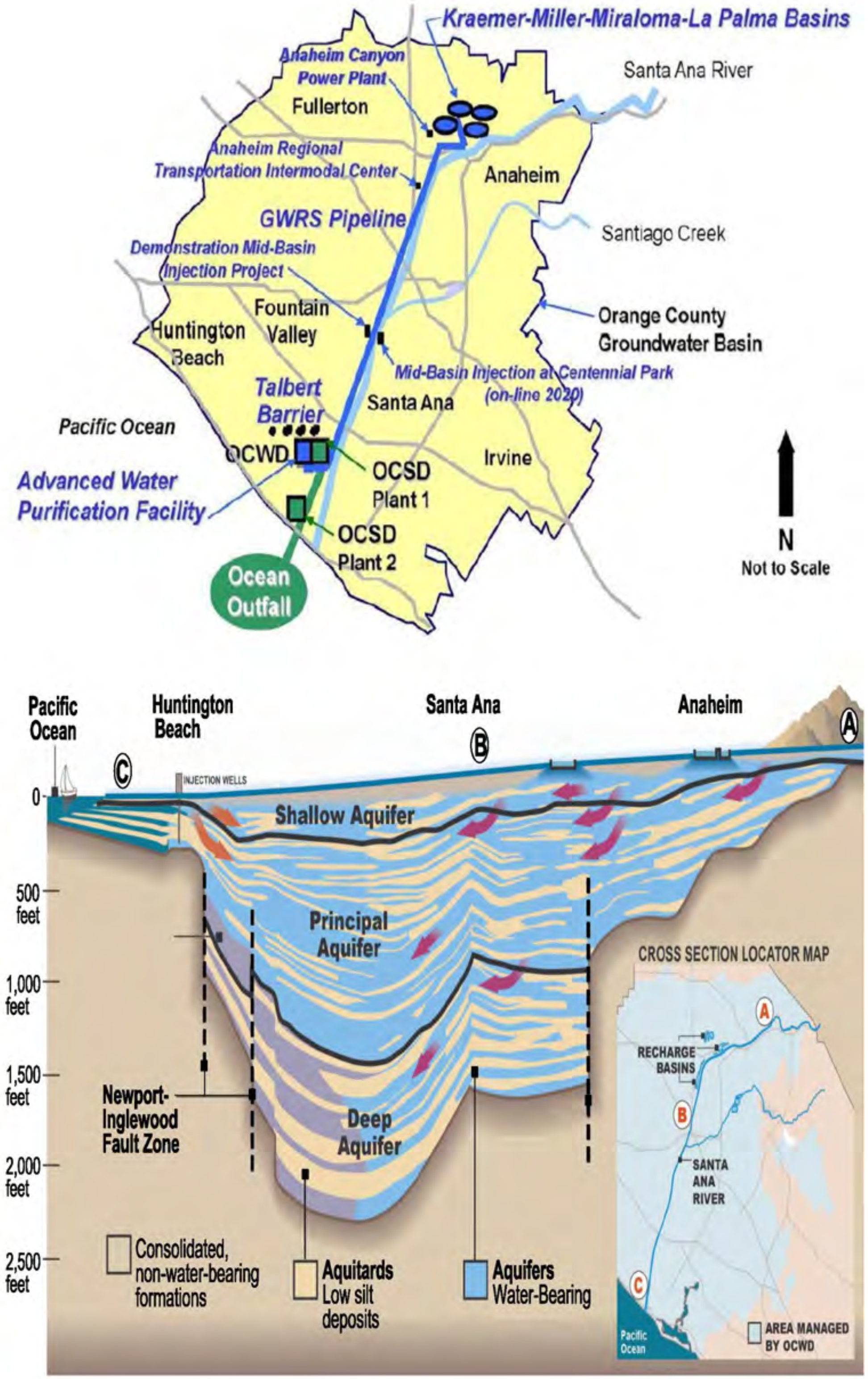
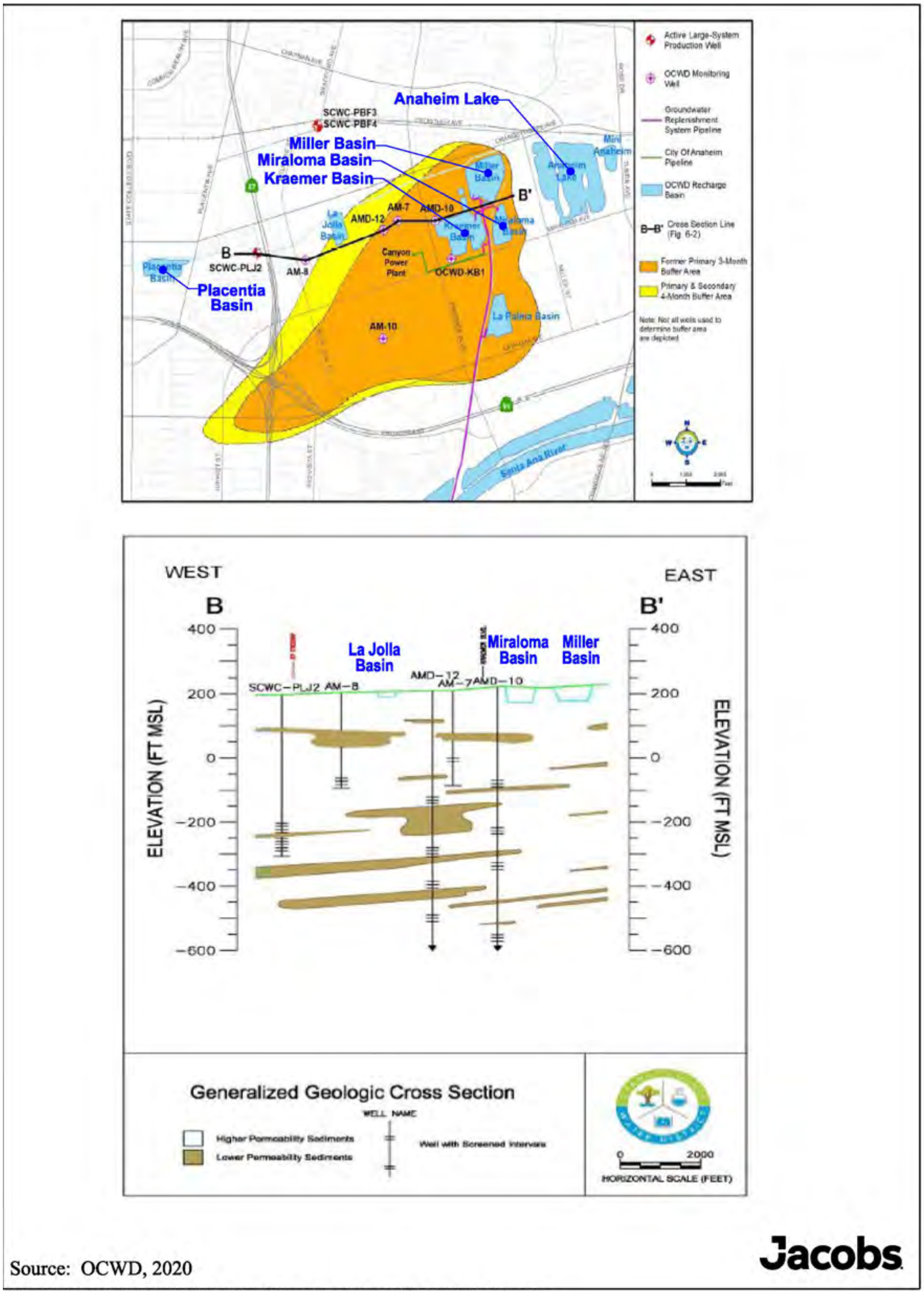


Figure 3-11. Location Map of OCWD MAR System.
Source: OCWD 2020.



Source: OCWD, 2020

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Figure 3-12. Section Line Map and Cross Section Near OCWD's Miraloma Basin.
Source: OCWD 2020.

Recharge

OCWD’s Groundwater Replenishment System project currently produces up to 100 MGD of high purity recharge by treating secondary-treated wastewater from the Orange County Sanitation District via microfiltration or UF (MF/UF), RO, and UV with hydrogen peroxide addition for advanced oxidation (Figure 3-13). Prior to recharge, OCWD stabilizes the recharge to protect distribution system piping using partial decarbonation and quicklime addition. The same recharge chemistry supplies the Talbert Seawater Intrusion Barrier injection wells, MBI wells, and spreading basins within the Forebay area. The Forebay area also receives MAR supplies from local Santa Ana River surface water, local stormwater runoff, and purchased raw imported surface water originating from either the Colorado River or the State Water Project via the Metropolitan Water District of Southern California.

Infiltration of high purity recharge into the Forebay area has resulted in transient spikes of arsenic at proximal monitoring wells. Arsenic concentrations and the frequency of its appearance diminishes with both time and distance from the MAR basins. Prior to infiltration the Groundwater Replenishment System recharge water does not contain detectable arsenic above the standard drinking water analytical method reporting limit of 1 µg/L. Native or antecedent groundwater in the Forebay area prior to the introduction of Groundwater Replenishment System recharge contained arsenic concentrations ranging from non-detect to 6 µg/L, varying spatially and with depth.

Recharge chemistry typifies water treated with MF/UF and RO followed by post-treatment stabilization, and thus exemplifies a likely chemistry that numerous MAR facilities will produce as the number of systems increase worldwide. The Groundwater Replenishment System project recharge water consists of dilute TDS concentrations, running less than 50 mg/L (Table 3-6 recharge and NGW), an alkaline pH (8.5) and mixed cation-bicarbonate (Figure 3-14). Containing near saturated concentrations of DO (8 to 10 mg/L) and measurable nitrate (0.8 to 1.3 mg/L), recharge displays an oxic redox with oxygen reduction representing the primary redox process. The performance of the Orange County Sanitation District nitrification treatment and the membranes at the Groundwater Replenishment System AWT both influence nitrate concentrations in recharge water.

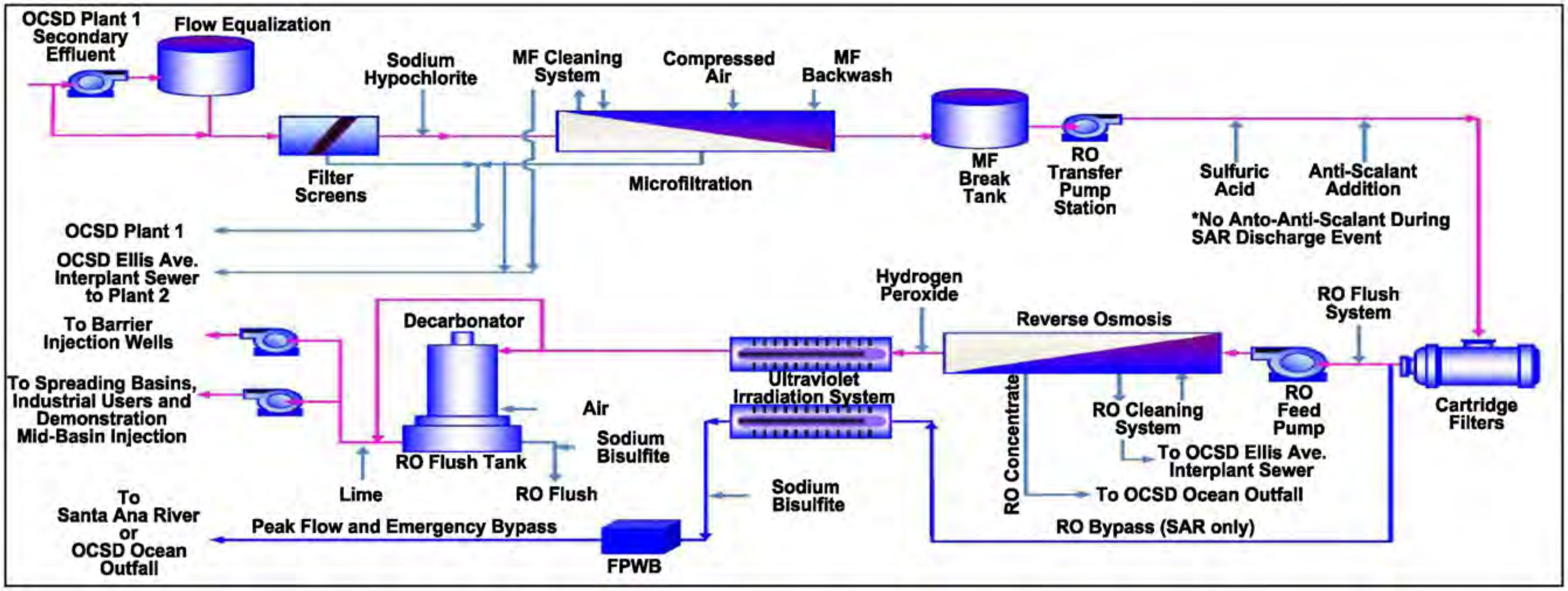
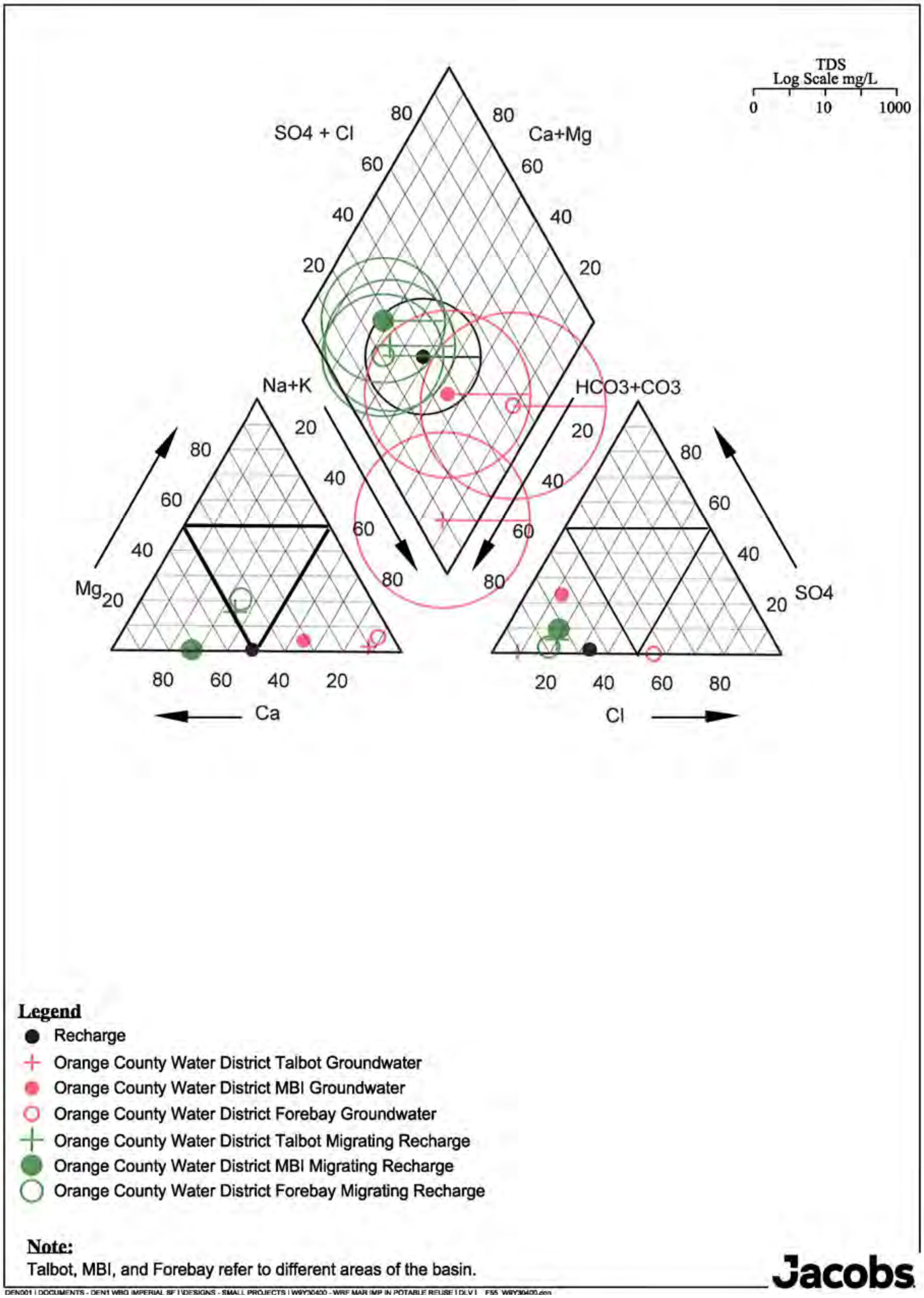


Figure 3-13. Treatment Processes at OCWD Advanced Water Treatment Facility.
Source: OCWD 2020.

Table 3-6. Summary of Water Quality at OCWD MAR Facility.

			Groundwater			Migrating Recharge		
Constituent	**Units**	**Recharge**	**Talbert**	**MBI**	**Forebay**	**Talbert**	**MBI**	**Forebay**
pH	standard units	8.5	8.22	8.1	9.2	7.7	7.3	7.9
Dissolved oxygen	mg/L	6.2	0.3	0.5	0.4	3	3.2	7
Calcium	mg/L	14	11	23	7	13	15	9
Magnesium	mg/L	0.25	1.5	1.9	5	3	0.05	3
Sodium	mg/L	6	105	52	134	10	6	7
Chloride	mg/L	5	14	14	121	7	5	5
Sulfate	mg/L	0.05[a]	0.3	36	0.1	3	4	1
Alkalinity	mg/L	38	243	126	160	51	38	41
Iron	mg/L	<0.01	0.2	0.01	NA	0.002	0.006	0.1
Manganese	mg/L	<0.001	0.02	0.1	NA	0.002	0.0001	0.003
Arsenic	mg/L	<0.001	0.0001	0.0002	NA	0.001	0.0001	0.002

[a] Concentration = half method detection limit



Note:
Talbot, MBI, and Forebay refer to different areas of the basin.

Figure 3-14. Piper Diagram Showing Ionic Composition of Recharge, Groundwater and Migrating Recharge for OCWD MAR Facility.

Groundwater—MAR Basin

Prior to the introduction of Groundwater Replenishment System water, groundwater in the surficial aquifer displayed TDS concentrations ranging from 200 to 650 mg/L in the Forebay area. TDS concentrations generally land in the fresh range with only concentrations from the Forebay area exceeding the SMCL of 500 mg/L. Groundwater displayed an alkaline pH around 8 and a sodium to mixed cation-bicarbonate chemistry, resembling the recharge. Total organic carbon (TOC) concentrations ranged from 1—2 mg/L. Forebay area groundwater redox properties generally match the Groundwater Replenishment System recharge as an oxic environment with oxygen reduction representing the primary redox process. Groundwater in the Talbert Seawater Barrier area falls in the anoxic redox category with methane reduction exemplifying the primary redox process (Table 3-4 redox assignments).

Groundwater—MAR Well

The ionic chemistry between Zones 1 through 3 appeared very similar with nearly identical concentrations of calcium, bicarbonate, chloride, and sulfide (Table 3-7). Instead, the groundwater chemistry varied according to how deep water from the overlying surficial aquifer penetrated into the three confined aquifers. Groundwater from Zone 1 displayed measurable concentrations of DO, nitrate, and phosphate, while concentrations of these constituents progressively diminished in Zones 2 and 3.

Although the publication does not provide iron and manganese concentrations in groundwater from Zones 1 through 3, the redox appears to range from oxic in Zone 1 to anoxic in Zone 3, while the representative redox processes comprise oxygen reduction in Zone 1 and potentially sub-oxic to ferric iron reduction in Zones 2 and 3. Sulfate concentrations in Zone 2 and 3 exceeding 50 mg/L suggest redox processes do not approach sulfate reducing conductions.

Table 3-7. Summary of Water Quality at OCWD's Test MAR Well Location.

			Groundwater		
Constituent	**Units**	**Recharge**	**Zone 1**	**Zone 2**	**Zone 3**
pH	standard units	8.6	7.6	7.5	7.6
Temperature	°C	26	20.5	20.5	20.5
Dissolved Oxygen	mg/L	6	2.88	0.13	0.00
Total organic carbon	mg/L	0.024	0.31	0.13	0.20
As	mg/L	<0.001	0.0020	<0.001	0.0020
Bicarbonate as $CaCO_3$	mg/L	39.65	197.03	197.03	197.03
Carbonate as $CaCO_3$	mg/L	1.98	0.00	0.00	0.00
Calcium	mg/L	10.025	45.11	45.11	45.11
Chloride	mg/L	11.088	16.26	17.56	16.63
Sulfate	mg/L	0.75955	60.76	64.87	71.09
Nitrate as N	mg/L	7.998	0.99	1.98	0.00
Phosphate as P	mg/L	0.028791	0.10	0.06	0.03

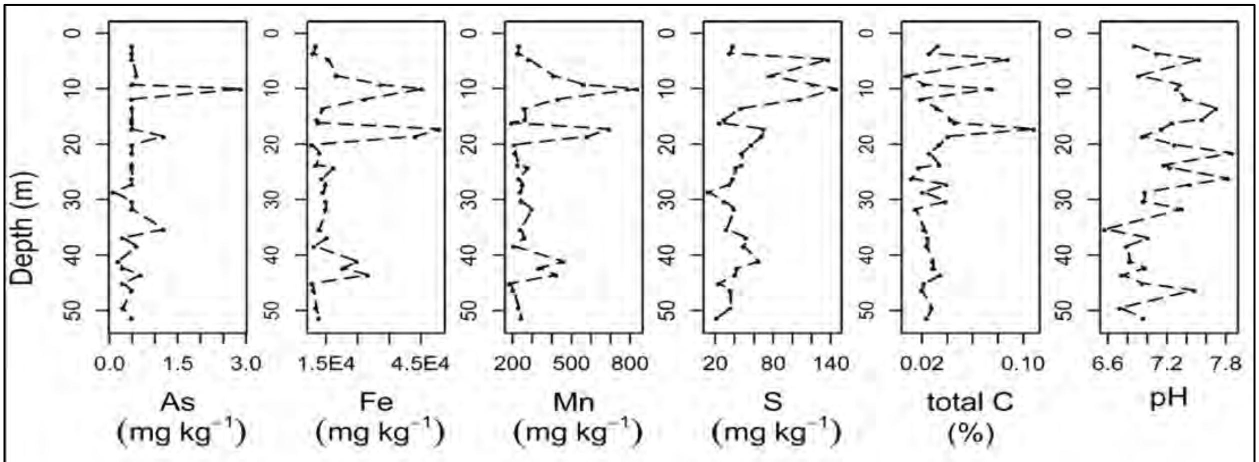
Aquifer Sediments

At the Miraloma Basin, OCWD installed a monitoring well featuring a screened interval extending from 138 to 148 fbg. Depth to groundwater is variable, ranging from 30 to 100 fbg with an average of approximately 50 fbg, demonstrating the influence of both season basinwide pumping and recharge cycles, as well as local recharge basin operations. Field personnel collected cores at roughly 2-foot intervals and submitted samples for the following laboratory analysis including:

- Bulk carbon and nitrogen analysis
- X-ray fluorescence (XRF) for bulk arsenic, manganese, iron and sulfide
- X-ray adsorption near-edge spectroscopy (XANES) to determine the oxidation state of arsenic
- Sediment pH
- X-ray diffraction (XRD) for clay mineral identification

Analysis of the aquifer sediments enabled OCWD to profile the abundance of elemental compositions and pH with depth (Figure 3-15). Maximum arsenic concentrations measured 2.9 milligram per kilogram (mg/kg), relatively low concentrations considering the global average for arsenic contained in soils and sediments ranges from 3 to 10 mg/kg (Shacklette and Boerngen 1984). The highest arsenic concentrations correlated with finer-grained horizons. These intervals also displayed the most elevated concentrations of other redox-sensitive elements including iron, manganese, and sulfide. Additionally, slightly greater carbon concentrations correlated with elevated arsenic. Sediment pH fluctuated around neutral and showed negligible correlation with constituent concentrations.

XRD analysis results revealed the clay fraction consisted mostly of vermiculite with small amounts of kaolinite. Arsenic appeared only in the clayey sediments, falling below MDLs for XRF analyses in coarser-grained sediments. In samples analyzed by XANES, arsenic appeared predominantly as arsenate (As V) and sediments displayed relatively low amounts carbon contained in the aquifer matrix. Moreover, arsenic concentrations in sediments displayed a low correlation coefficient with bulk carbon.



Source: Fakhreddine, et. al., 2015

Figure 3-15. Composition of Aquifer Sediments in Test Boring for Orange County Groundwater Replenishment System.

Migrating Recharge—MAR Basin

Migrating recharge, defined above as recharge water after entering the aquifer(s) through a well or basin, from the differing sectors features a circumneutral pH ranging from 7.3 to 7.9, slightly more acidic than the recharge pH at 8.5. Migrating recharge displays a calcium to mixed cation—bicarbonate chemistry resembling recharge. Except for the Forebay sector, migrating recharge displays oxic to suboxic redox conditions with oxygen reduction representing the primary redox process. Like the groundwater chemistry, migrating recharge found beneath the Forebay displays a mixed anoxic redox conditions with ferric iron reduction defining the main redox process (Table 3-4).

In summary, migrating recharge from the MAR Basin shows minimal long-term changes in water chemistry compared to the chemistry of recharge entering the aquifers. The more acidic pH suggests modest amounts of sulfide oxidation with the production of acid. The spikes in arsenic concentrations appear to originate from mechanisms related to cation bridging with clay minerals as described in one of the case studies unrelated to acid-base or redox reactions.

Migrating Recharge—MAR Well

As mentioned previously, the MAR well recharge water to three confined aquifer zones (Figure 3-16) DO concentrations recovered at monitoring wells screening Zone 1 and 3 decline to below MDL’s in migrating recharge. By contrast, DO increases in Zone 2 to concentrations equivalent to the recharge water. In addition to the varying hydraulics between the three zones and predominance of Zone 3 for accepting water, the publication indicates that the presence of pyrite in Zones 1 and 3 diminishes DO recovered in the monitoring wells through pyrite oxidation.

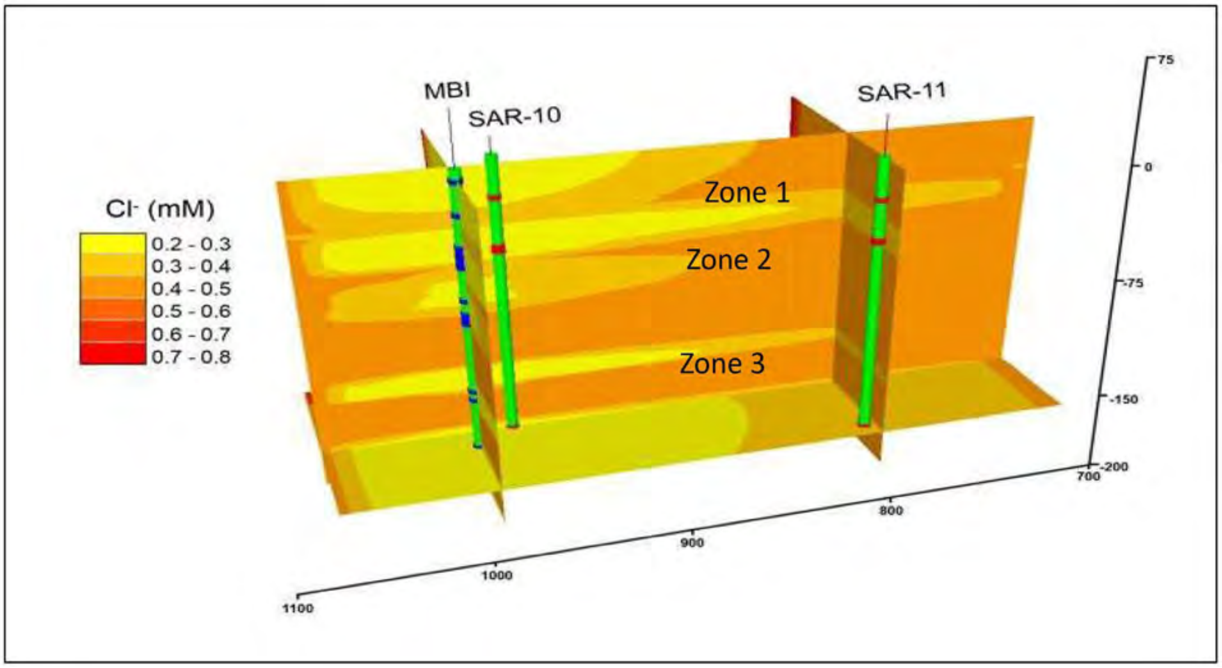


Figure 3-16. Cross Section Showing Injection Well (MBI) and Associated Monitoring Wells.

Except for the emergence of arsenic, pyrite oxidation does not appear to influence the concentrations of other constituents in the migrating recharge. Typically, during pyrite oxidation, pH, and alkalinity decline while iron, and possibly manganese and sulfate, concentrations increase (Evangelou 1995). Yet, concentration—time series graphs from the monitor wells show little perceptible change in pH, alkalinity, or sulfate. The presence of calcite in the aquifer sediments may buffer the pH and alkalinity, however the conservative behavior of sulfate seems unusual.

In Zones 1 through 3 arsenic concentrations increase in migrating recharge time coincident with the arrival of recharge at each monitoring well with the highest concentrations approaching 8 µg/L in Zone 1. After the initial increase, arsenic concentrations decline to background concentrations in Zones 2 and 3 within three to five months, while arsenic remains elevated above background in Zone 1. Fakhreddine (Fakhreddine et al. 2020) attributes declining arsenic in Zones 2 and 3 to its rapid depletion in aquifer sediments and within the atomic structure of arsenian pyrite. Moreover, progressive precipitation of HFO surfaces may adsorb arsenic in migrating recharge.

3.2.1.6 Tucson Water

The Tucson Water Clearwater Program (TWCP; Figure 3-17) recharges up to 134 MGD of Colorado River water through 20 basins into the Avaro Aquifer, a regional alluvial aquifer system, which can exceed a thickness of 1,000 feet. Thus, the TWCP program does not follow some of the criteria required for an indirect potable reuse system as dictated by the constraints of the project. Yet, TWCP provided a thoroughly prepared utility survey and follow-on interview. The recharge water, groundwater, and migrating recharge water chemistry provides a clear portrayal of recharging water into alluvial aquifers below a desert environment.

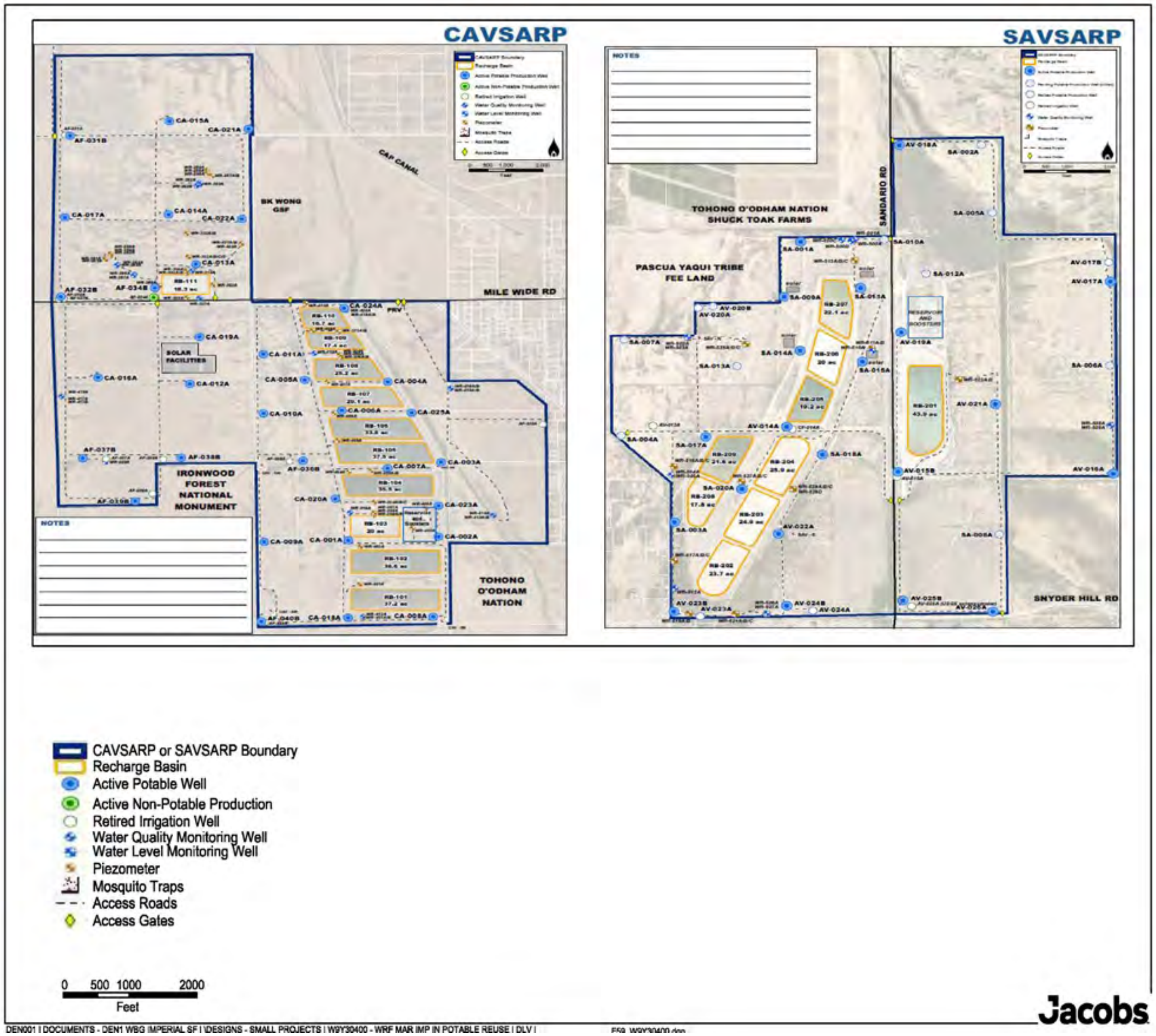


Figure 3-17. Location Maps of Tucson Water's CAVSARP and SAVSARP Projects.

TWCP separates the system into two sections comprising the Central Arva Valley Storage and Recovery Project (CAVSARP) and the Southern Arva Valley Storage and Recovery Project areas. Composed of gravels interbedded with discontinuous clay confining beds the transmissivity of the Avaro Aquifer ranges from 1,000 to 40,000 ft^2/d. The static water level marks the top of the unconfined aquifer and lies 160 fbg providing a thick vadose zone.

Recharge Chemistry

Recharge from TWCP's Colorado River allocation exhibited an alkaline recharge featuring a pH around 8.4 and TDS concentrations in the fresh range at 590 mg/L (Table 3-8). Recharge displayed a mixed cation—mixed anion, sulfate (Figure 3-18) chemistry. Although not entered in the survey form, recharge likely contained near saturated concentrations of DO, categorizing the redox as oxic and oxygen reduction as the primary redox process.

Table 3-8. Summary of Water Quality at Tucson Water Facility.

			Groundwater	Migrating Recharge
Constituent	**Units**	**Recharge**	**Alluvium**	**Alluvium**
pH	standard units	8.4	8	7.8
Dissolved oxygen	mg/L	NA	NA	NA
TDS	mg/L	590	190	584
Calcium	mg/L	69	23	110
Magnesium	mg/L	28	3	15
Sodium	mg/L	92	36	55
Chloride	mg/L	91	8	95
Sulfate	mg/L	219	9	55
Alkalinity	mg/L	123	131	184
Iron	mg/L	0.02	<0.02	<0.03
Manganese	mg/L	<0.02	NA	<0.02
Arsenic	mg/L	0.003	0.007	0.002

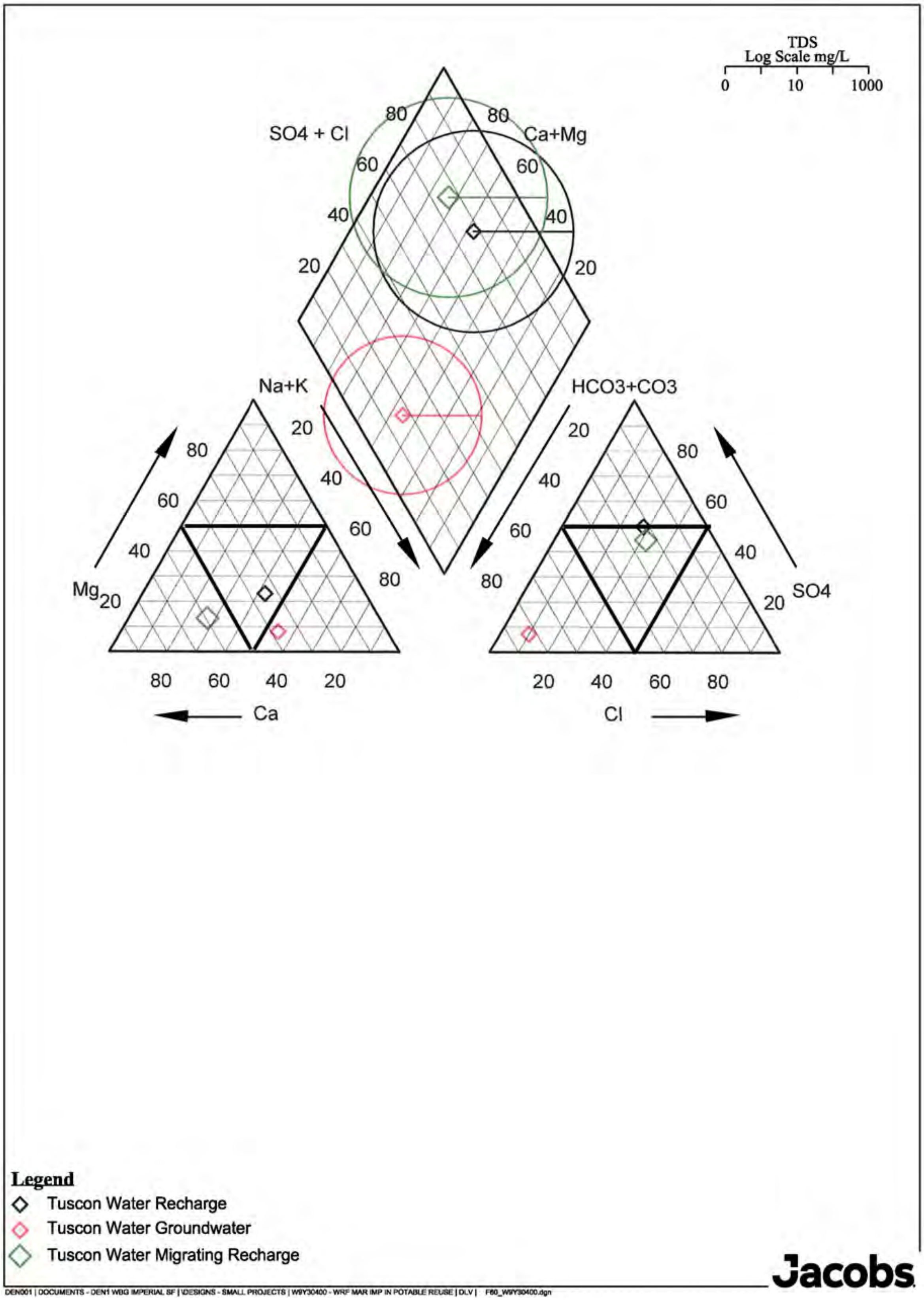


Figure 3-18. Piper Diagram Showing Ionic Composition of Tucson Water Recharge, Groundwater and Migrating Recharge.

Groundwater Chemistry

Groundwater from the Avaro Aquifer displayed an alkaline pH around 8, TDS concentrations consistent with fresh water (less than 200 mg/L) and a calcium bicarbonate chemistry. Thus, TWCP's MAR facility represents one of the few systems that recharges water containing a higher TDS and ionic strength into groundwater displaying lower TDS/ionic strength. Groundwater from the Avaro Aquifer displayed anoxic conditions with nitrate reduction describing the primary redox process.

Migrating Recharge Chemistry

Except for the main cation, migrating recharge displayed a similar chemistry to the recharge prior to infiltration. Migrating recharge exhibited a pH slightly less than 8 and nearly identical TDS concentrations to the recharge. However, migrating recharge featured a calcium—mixed anion water compared to the mixed cation-sodium-mixed anion-sulfate recharge chemistry. The more calcic chemistry infers some amount of cation exchange between sodium in the recharge and calcium in the exchange position of clays. Sodium concentrations in the migrating recharge were nearly half compared to concentrations in the recharge. Migrating recharge displayed an anoxic redox with nitrate reduction defining the primary redox process.

3.2.1.7 Water Replenishment District of Southern California

WRD manages the West Coast and Central Basins of the Los Angeles Basin, and jointly operate a MAR facility containing 30 basins that recharge more than 100 MGD. The basins are positioned along unlined reaches of the San Gabriel River (San Gabriel Coastal Spreading Grounds) and Rio Hondo River (Rio Hondo Coastal Spreading Grounds) in the Montebello Forebay of the Central Basin (Figure 3-19).

The area exhibits ideal conditions that favor recharge into unconfined, transmissive alluvial soils that allow recharge directly to seven local aquifers (Gaspur, Gage, Gardena, Lynwood, Silverado, Sunnyside, and Pico Formation) and indirect recharge to three additional aquifers (Exposition-Artesia, Hollydale, and Jefferson). The benefits of recharge in the Montebello Forebay include restoring overdrawn groundwater levels, improving groundwater quality, mitigating land subsidence, and recovery as a drinking water supply downgradient in the Central Basin.

Recharge activities started in the Montebello Forebay in the late 1950s and continue until present day. Recharge supply has historically come from a variety of sources, including stormwater, imported water, tertiary treated recycled water, and recently AWT from the newly constructed Albert Robles Center (ARC) Facility. Recharge rates have averaged 100 MGD over the last 10 years, with approximately 14.8 MGD consisting of AWT from the ARC Facility. The amount and water quality characteristics of the recharge have varied widely over the period, primarily due to annual variations in stormwater quality and blending requirements with tertiary treated water. Annual and seasonal variations in recharge water quality makes it difficult to compare recharge and groundwater quality characteristics. WRD did not report recovery of any undesirable geogenic constituents in downgradient groundwater supply or monitoring wells.

Figure 3-19. Location of Montebello Spreading Grounds and Leo J. Vander Lans Advanced Water Treatment Facility.
Source: Modified from WRDSC 2021.

3.2.2 Utilities in Planning

This section discusses the characteristics of MAR utilities in planning. As many of the MAR facilities have not undergone extensive evaluation, the sections contain less detail than sections discussing the operating facilities. Most surveys contained the recharge and groundwater, but none of the study participants have yet to run a pilot test producing migrating recharge water chemistry. Moreover, recharge chemistry carries one of two origins, either reported from an existing AWT that will also service the facility in planning, or represents chemistry estimated by mathematical simulations using secondary wastewater and the assumed AWT processes.

As several planning efforts (Valley Water and Pure Water Soquel) have entered only their earliest phases, sufficient information does not appear available to accurately portray the nature of the developing facility.

3.2.2.1 Water Corporation—Woodman Point

Like the Beenyup Groundwater Replenishment Scheme, WC plans on recharging the Leederville and Yarragadee Aquifers with water sourced from the Woodman Point wastewater treatment plant in Munster, south of Perth, Western Australia. Initial conversations with WC's scientists indicate the recharge chemistry will involve water treated with MF/UF and RO and thus its chemistry is expected to resemble the recharge produced from the Beenyup Groundwater Replenishment Scheme. The relatively dilute chemistry of the recharge (Table 3-9; TDS 25 mg/L) differs significantly from the brackish groundwater found in the Leederville and Yarragadee Aquifers where groundwater exhibits TDS concentrations exceeding 1,500 mg/L. Ionic strengths for the water types run 6E-4, 4E-2 and 5E-2 for the recharge and groundwater from the Leederville and Yarragadee Aquifers, respectively. Thus, the ionic strength of the groundwater exceeds the recharge by two orders of magnitude. Groundwater from the Leederville and Yarragadee Aquifers at the Beenyup Groundwater Replenishment Scheme did not exhibit ionic strengths that differed by two orders of magnitude from the recharge water.

Table 3-9. Summary of Water Quality at WC Woodman's Point MAR Facility in Planning.

			Groundwater	
Constituent	**Units**	**Recharge**	**Leederville**	**Yarragadee**
pH	standard units	7.22	7.2	7.6
Dissolved oxygen	mg/L	8	NA	NA
TDS	mg/L	24	1610	2030
Calcium	mg/L	0.05 1	45	34
Magnesium	mg/L	0.05 1	30	26
Sodium	mg/L	8.1	464	631
Chloride	mg/L	6	760	985
Sulfate	mg/L	0.05[a]	82	80
Alkalinity	mg/L	9	180	229
Iron	mg/L	<0.01	2	0.3
Manganese	mg/L	<0.001	0.03	0.03
Arsenic	mg/L	<0.001	<0.002	NA

[a] Concentration= 1/2 method detection limit

As mentioned previously, a difference of one order of magnitude between recharge and groundwater prompts concerns for clay swelling, fragmentation, dispersion, migration and pore clogging causing often catastrophic, irreversible reductions in the intrinsic permeability of the receiving aquifer. WC observed an increase in total aluminum concentrations at a nearby monitoring well, attributing the increasing concentrations to kaolinite in the sample, and possibly evidence of clay dispersion.

Before recharging water treated with UF and RO into the Leederville and Yarragadee Aquifers, WC should consider either a different treatment process for recharge that produces a less dilute chemistry, or treating the Leederville and Yarragadee Aquifers around each MAR well with Al-salts to stabilize clay minerals. Conditioning requires several weeks and 300,000 to 600,000 gallons of Al-salt solution.

The recharge and groundwater from the Leederville and Yarragadee Aquifer also display sodium chloride water (Figure 3-20), so cation exchange should not constitute a concern during MAR operations. Groundwater from the Leederville and Yarragadee Aquifers exhibit modest to elevated concentrations of iron at 0.25 to 2.1 mg/L, respectively, while arsenic concentrations were below laboratory MDLs.

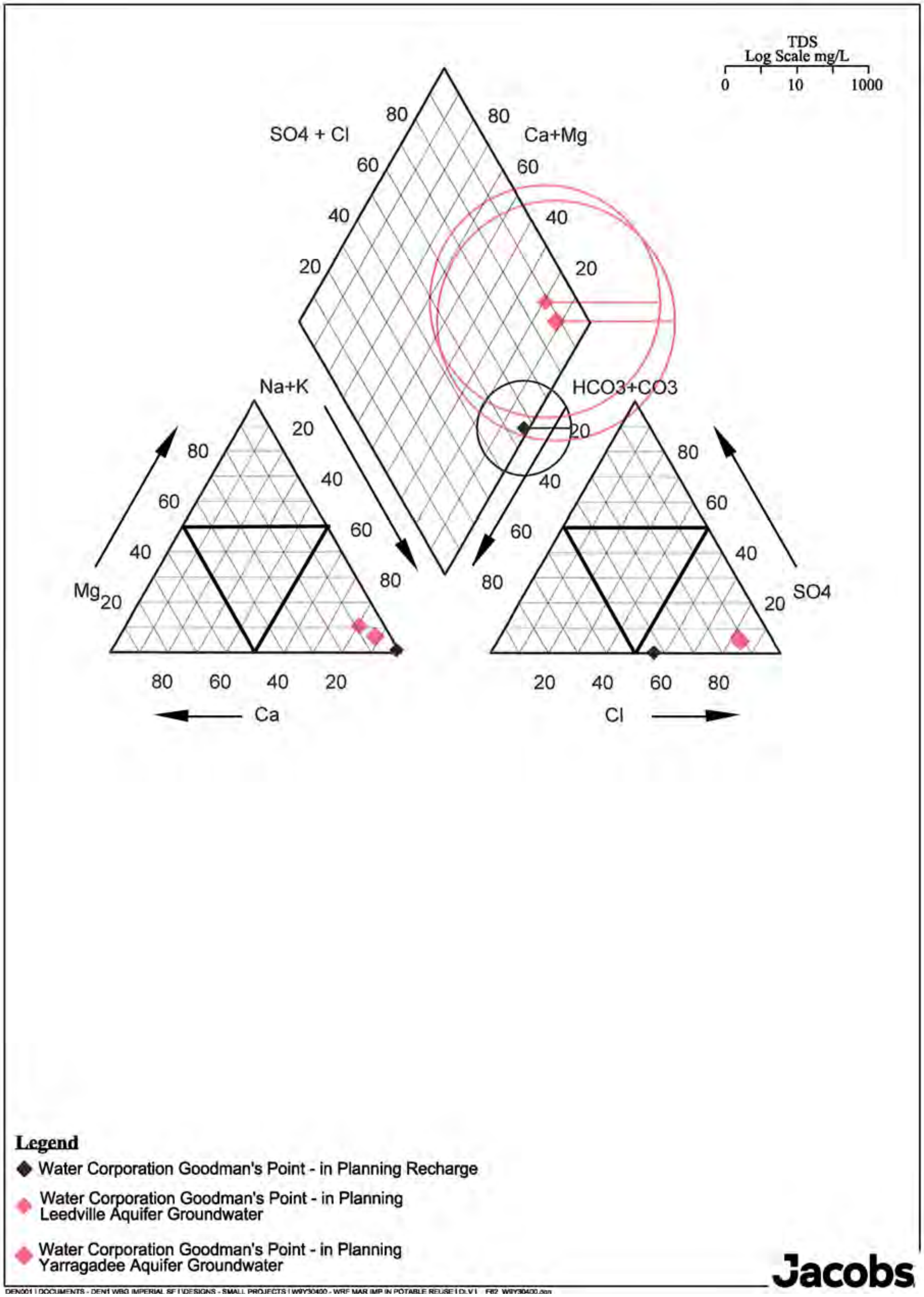


Figure 3-20. Piper Diagram Showing Ionic Composition of Recharge of Groundwater at the Water Corporation's Woodman Point Facility.

3.2.2.2 Tri-Valley Agencies

The Tri-Valley Agencies, consisting of California Water Service, the City of Livermore, the City of Pleasanton, Dublin San Ramon Services District, and Zone 7 Water Agency, are located in the Livermore-Amador Valley, California (Figure 3-21) and are evaluating MAR in a shallow Holocene-Age alluvium sand aquifer through surface spreading and wells. The unconfined Livermore Groundwater Basin Aquifer (LBGWBA) beneath the area extends to 100 fbg with the static water level hovering around 50 fbg defining the top of the aquifer and the vadose zone thickness. The Tri-Valley Agencies plan to recharge via surface spreading in two former quarries/lakes and installing up to 10 wells for direct injection at the site.

The Tri-Valley Agencies provided an estimated recharge chemistry in their survey (Table 3-10). Recharge will display a circumneutral to mildly alkaline pH around 7.8 with TDS concentrations of 580 mg/L and sodium-mixed anion chemistry (Figure 3-22). The survey suggested that iron concentrations in the recharge might equal around 0.3 mg/L. Iron concentrations exceeding 0.1 mg/L in recharge imposes a strong clogging potential on MAR well and basins. Thus, to the extent practical utilities should remove iron and manganese to concentrations less than 0.1 and 0.01 mg/L, respectively, from recharge.

Table 3-10. Summary of Water Quality at Tri-Valley Agencies in Planning MAR Facility.

			Groundwater
Constituent	**Units**	**Recharge**	**Alluvium**
pH	standard units	7.8	7.7
Dissolved oxygen	mg/L	NA	NA
TDS	mg/L	580	500
Calcium	mg/L	33	42
Magnesium	mg/L	19	37
Sodium	mg/L	140	30
Chloride	mg/L	180	63
Sulfate	mg/L	59	35
Alkalinity	mg/L	317	190
Iron	mg/L	0.32	<0.1
Manganese	mg/L	0.027	<0.01
Arsenic	mg/L	NA	<0.001

NA = Not analyzed

Groundwater in the LBGWBA displayed circumneutral pH around 7.7, TDS concentrations approaching 500 mg/L and mixed cation, magnesium—bicarbonate water. Concentrations of iron, manganese, and arsenic fall below MDL. Nitrate concentrations approach 8 mg/L a relatively elevated value for groundwater. Yet, the elevated value suggests a hydraulic connection with the ground surface and infers relatively oxic redox conditions in the LBGWBA.

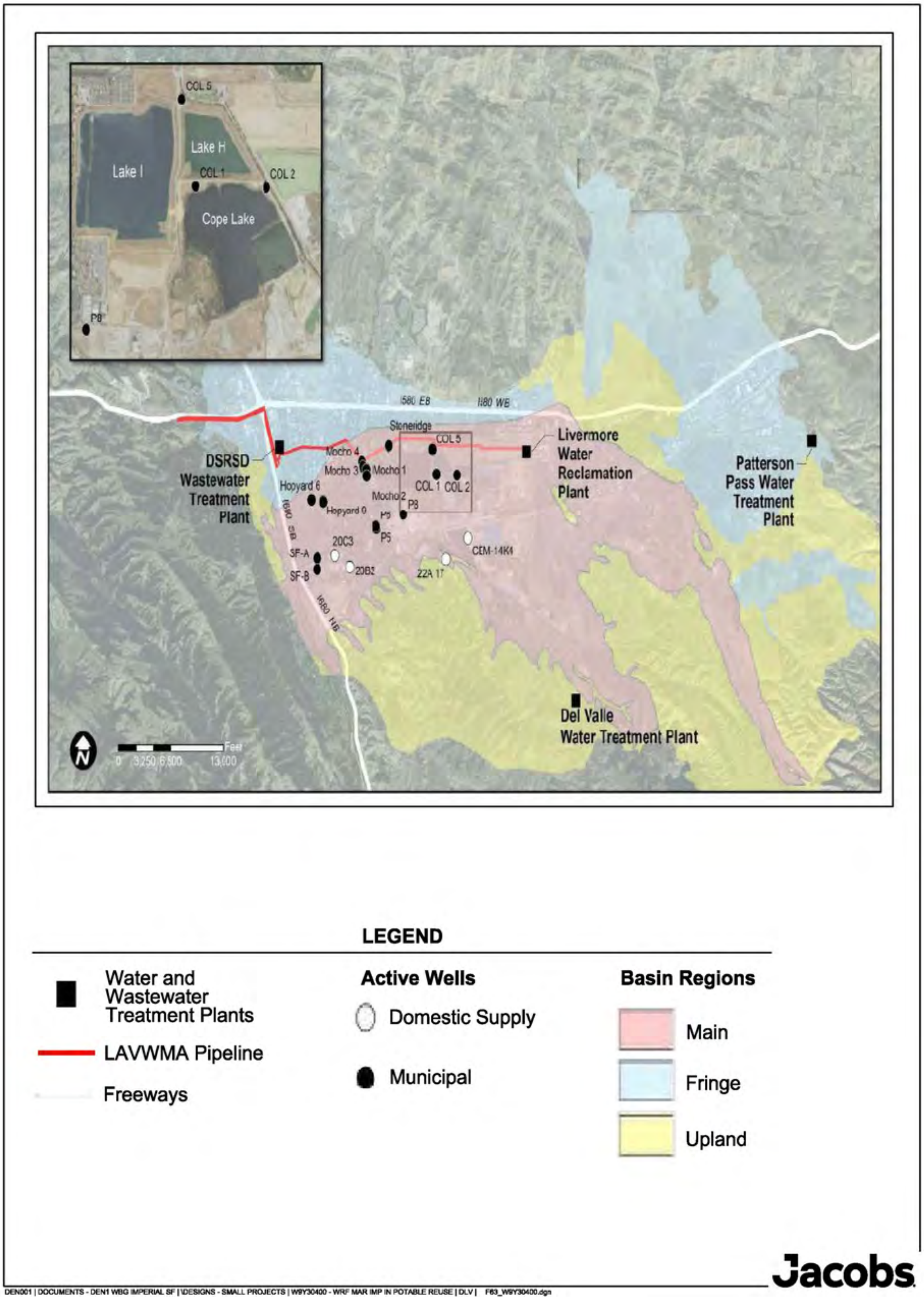
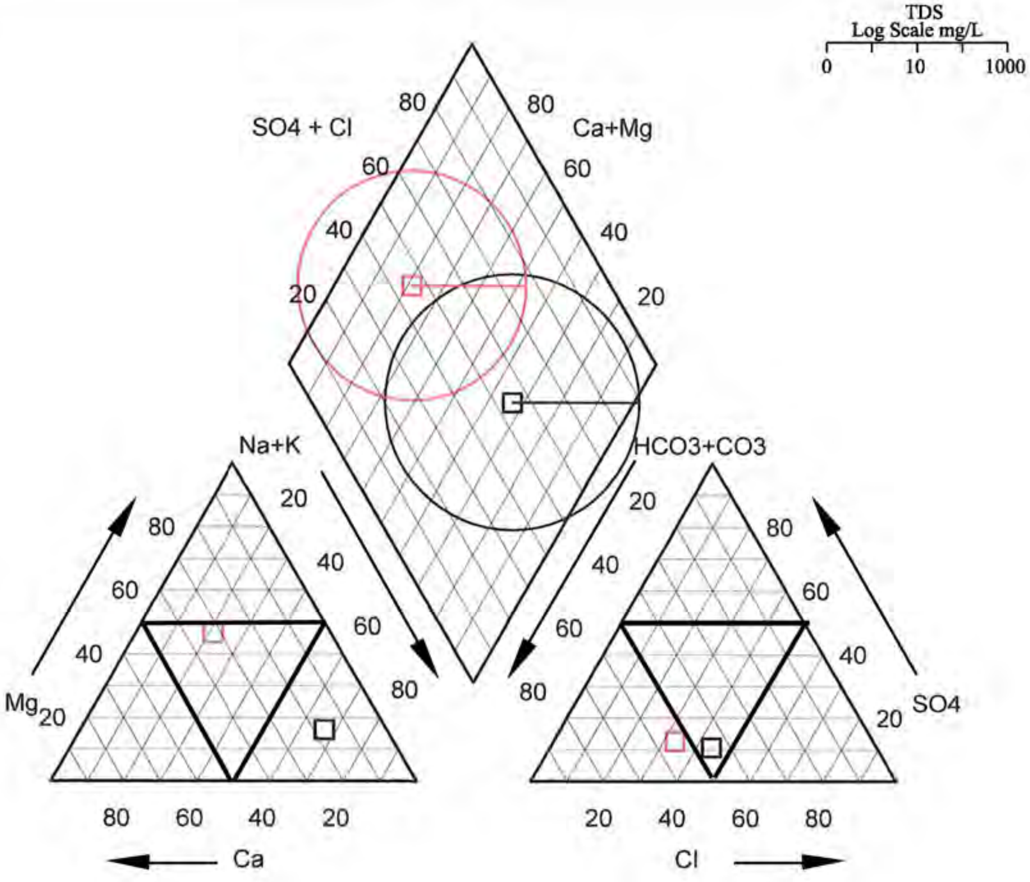


Figure 3-21. Location Map of Tri-Valley Agency's MAR Facility in Planning.



Legend

☐ Tri-Valley Zone 7 Recharge

☐ Tri-Valley Zone 7 Groundwater

Note:
Facility currently in planning so no migrating recharge chemistry available.

Jacobs

DEN001 | DOCUMENTS - DEN1 WBG IMPERIAL SF | \DESIGNS - SMALL PROJECTS | W9Y30400 - WRF MAR IMP IN POTABLE REUSE | DLV | F64_W9Y30400.dgn

Figure 3-22. Piper Diagram Showing Ionic Composition of Recharge and Groundwater for Tri-Valley Agencies MAR Facility in Planning.

3.2.2.3 Anne Arundel County

AACo Department of Public Works located in Annapolis, Maryland (Figure 3-23) plans on developing a MAR facility at their Patuxent Water Reclamation Facility (PWRF). The facility will retain a capacity of 8 MGD and require up to 10 MAR wells each capable of recharging 0.5 to 1.0 MGD each. Like HRSD in Virginia, AACo will recharge AWT effluent to the upper, middle and lower zones of the Cretaceous-Age PAS aquifer system, which below PWRF ranges in depth from 110 to 1,010 fbg. The PAS consists of interbedded, unconsolidated sands and clays. All three aquifer zones appear confined and display transmissivities ranging from 3,100 to 5,200 ft^2/d.

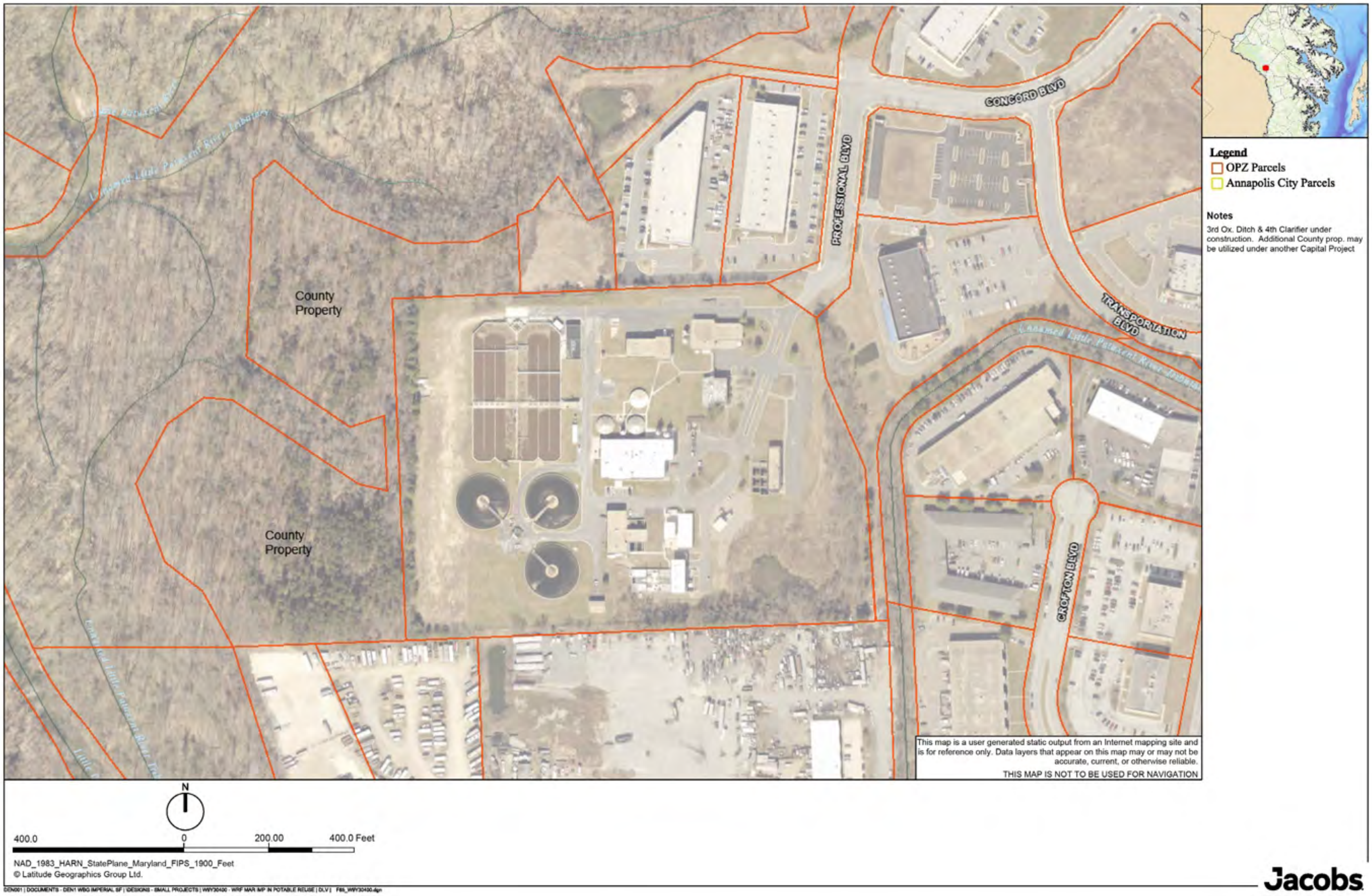
AACo mathematically simulated the chemistry of recharge based on the assumed AWT treatment processes including floc/sed, ozonation, BAC, GAC, and a combination of ultraviolet and chlorine or chloro-amines for disinfection. Recharge should display an alkaline pH around 8, concentrations of TDS of 230 mg/L (Table 3- 11) and sodium-mixed anion chemistry. Recharge will contain DO concentrations of 8 mg/L, or greater characterizing the recharge as oxic with oxygen reduction representing the primary redox process (Table 3-4 Redox).

Table 3-11. Summary of Water Quality at AACo MAR Facility in Planning.

			Groundwater
Constituent	**Units**	**Recharge**	**PAS**
pH	standard units	8	4.5 to 6.1
Dissolved oxygen	mg/L	8	0.01
TDS	mg/L	230	17 to 31
Calcium	mg/L	20	0.4 to 3.2
Magnesium	mg/L	5	0.2 to 2
Sodium	mg/L	50	0.8 to 2
Chloride	mg/L	45	0.9 to 1.7
Sulfate	mg/L	35	0.8 to 2
Alkalinity	mg/L	80	4.7 to 16
Iron	mg/L	0.01	0.3 to 3.1
Manganese	mg/L	0.012	0.04 to 0.1
Arsenic	mg/L	0.0001	0.005

Groundwater from the PAS system beneath the PWRF displayed dilute concentrations of TDS ranging from 17 to just over 30 mg/L and acidic pH ranging from 4.5 to 6.1. Groundwater displayed a mixed cation sulfate chemistry (Figure 3-24). The predominance of sulfate infers that active pyrite oxidation controls the ionic chemistry of groundwater. Iron concentrations range up to 3 mg/L with arsenic concentrations around 0.005 mg/L, above the MDL, but below the Maryland PMCL of 0.010 mg/L. Evaluation of redox species indicates mixed oxic-anoxic conditions with nitrate and ferric iron reduction characterizing the primary redox processes.

The presence of elevated iron, arsenic, sulfate, and acidic pH concentrations suggests pyrite oxidation controls the chemistry of groundwater in the PAS. Accordingly, AACo will need to take pretreatment measures to passivate pyrite in situ or remove oxidants from the recharge to prevent further oxidation.



Notes

3rd Ox. Ditch & 4th Clarifier under construction. Additional County prop. may be utilized under another Capital Project

This map is a user generated static output from an Internet mapping site and is for reference only. Data layers that appear on this map may or may not be accurate, current, or otherwise reliable.

THIS MAP IS NOT TO BE USED FOR NAVIGATION

Figure 3-23. AACo's Patuxent WRF Site.

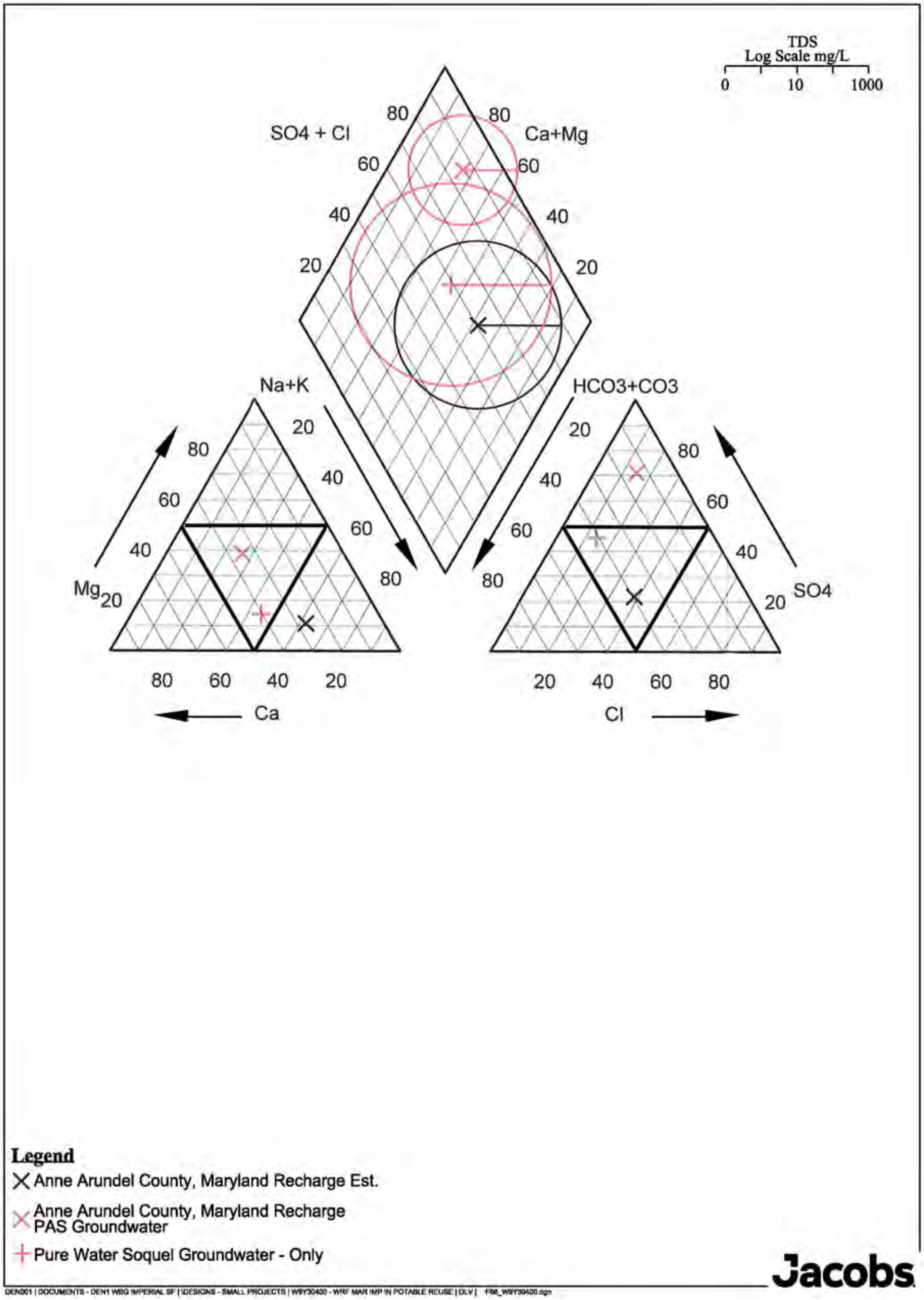


Figure 3-24. Piper Diagram Showing Major Tonic Composition for Recharge and Groundwater at Planned MAR Facility for AACo.

3.2.2.4 Valley Water

Valley Water located in Campbell, California (Figure 3-25) is investigating the feasibility of developing a MAR facility that will recharge up 30 MGD through basins into a Quaternary Age unconfined aquifer underlying the Santa Clara Groundwater Subbasin of the Santa Clara Valley groundwater basin. The unconfined aquifer composed of interbedded sand and gravel with discontinuous clay confining beds extends from the static water level, found at 40 fbg to 1,000 fbg. As determined by aquifer testing, the aquifer displayed a transmissivity ranging from 10,000 to 15,000 ft^2/d.

The recharge water chemistry, presumably estimated through mathematical simulation consists of an alkaline pH around 8, TDS concentrations slightly greater than 100 mg/L (Table 3-12), and a sodium chloride chemistry (Figure 3-26). Recharge exhibits near saturated concentrations of DO approaching 9 mg/L and nitrate concentrations around 2 mg/L, characterizing the recharge as oxic and oxygen reduction as the primary redox process.

Table 3-12. Summary of Water Quality at Valley Water MAR Facility in Planning.

			Groundwater
Constituent	**Units**	**Recharge**	**Quaternary Alluvial Deposits**
pH	standard units	8	7.6
Dissolved oxygen	mg/L	8.7	2.8
TDS	mg/L	106	410
Calcium	mg/L	16	66
Magnesium	mg/L	0.04	28
Sodium	mg/L	26	31
Chloride	mg/L	36	46
Sulfate	mg/L	0.3	44
Alkalinity	mg/L	39	240
Iron	mg/L	<0.02	22
Manganese	mg/L	<0.02	13
Arsenic	mg/L	<0.0005	<0.002

Groundwater in the surficial aquifer displays a circumneutral to slightly alkaline pH around 7.6, and TDS concentrations in the fresh range at 410 mg/L. Groundwater displays a mixed cation, calcium-bicarbonate chemistry typical of water receiving meteoric water as recharge. Redox species exhibit some disequilibrium including highly elevated iron concentrations around 22 mg/L and nitrate concentrations near MDLs in the presence of oxic concentrations of DO approaching 3 mg/L. Ignoring the DO concentrations around 3 mg/L, which likely represent an artifact of leaking tubing, groundwater displays an anoxic redox with iron reduction exemplifying the primary redox process. Arsenic concentrations in groundwater fall below MDLs.

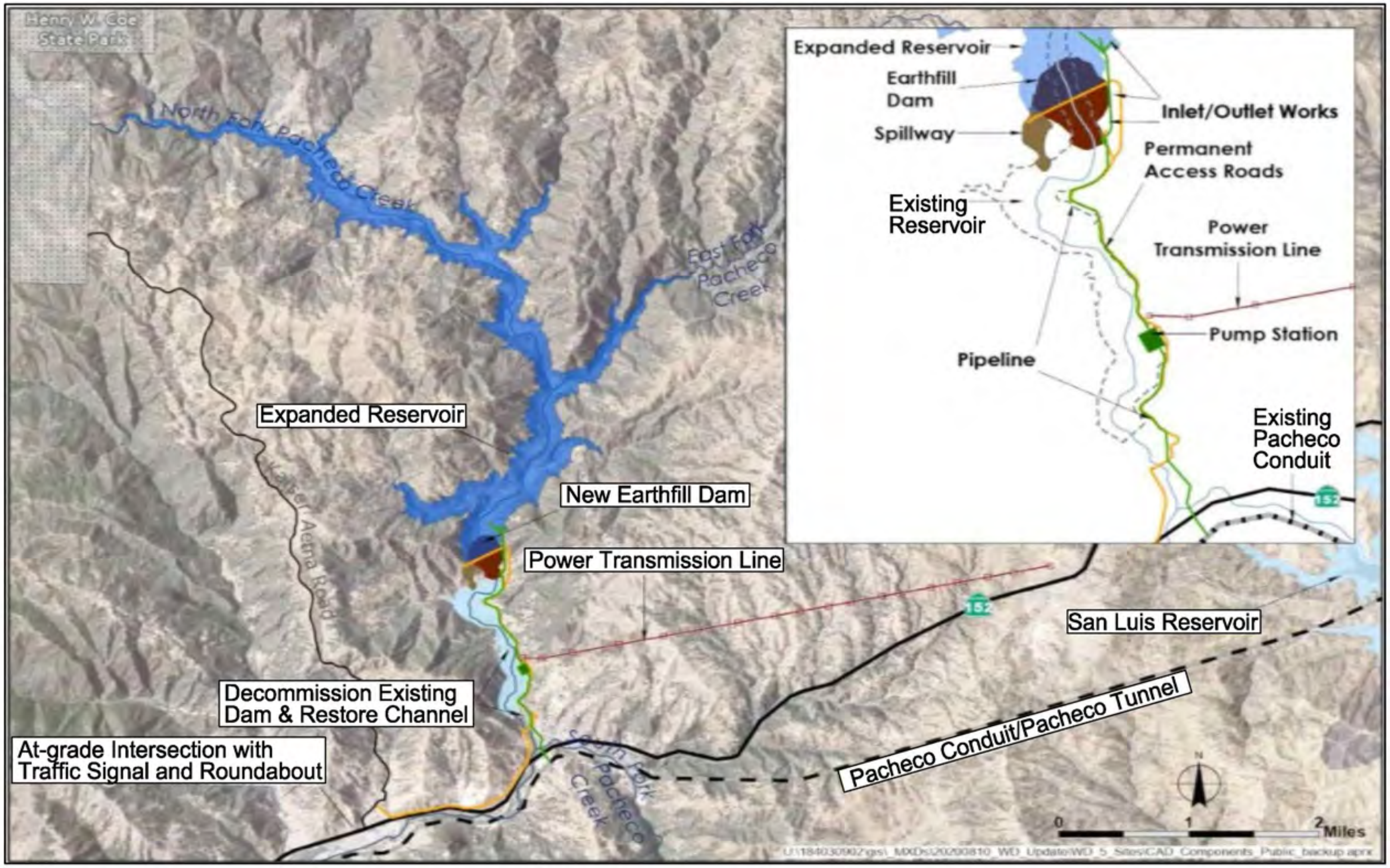


Figure 3-25. Location Map of Valley Water, Santa Clara, California.

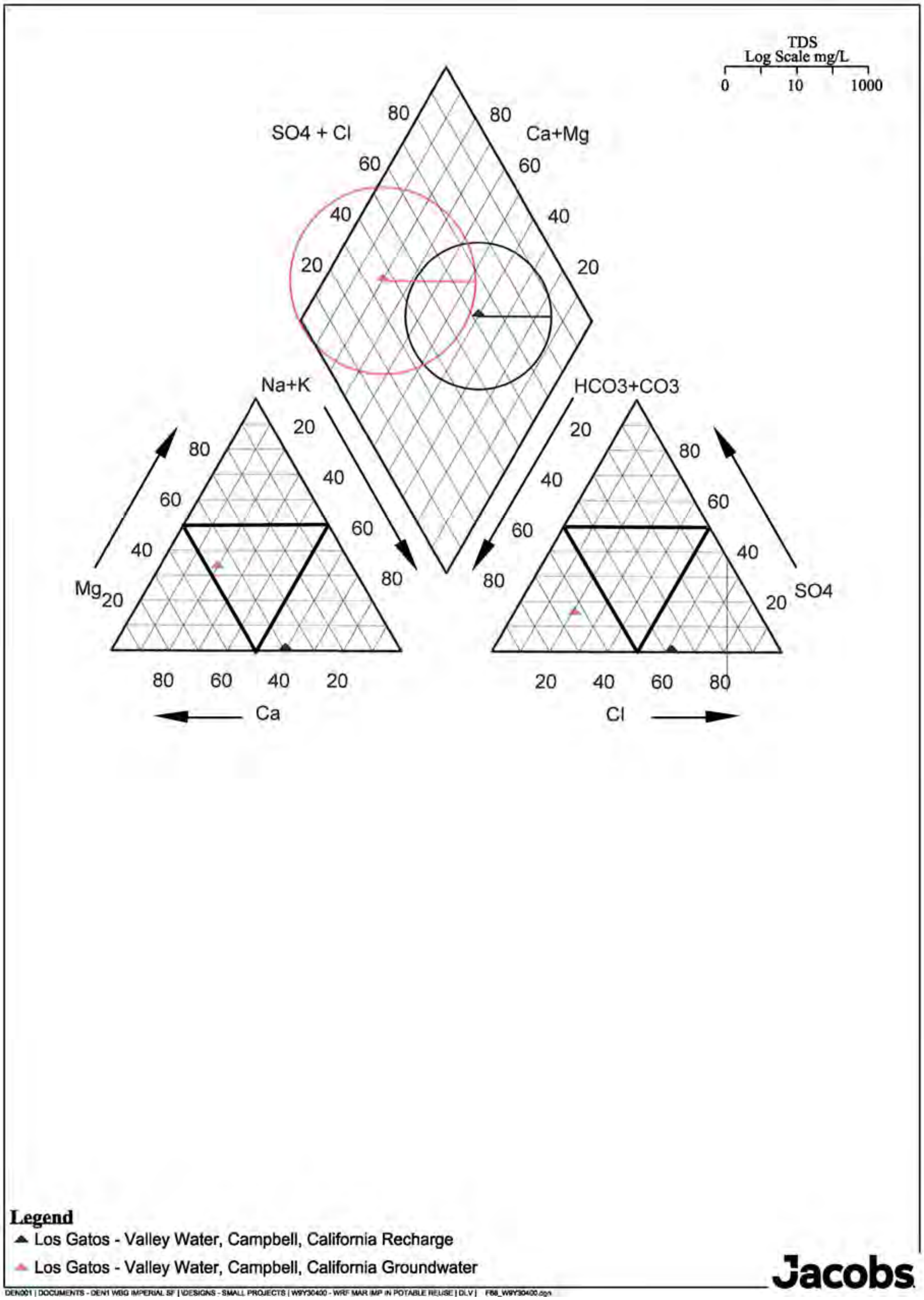


Figure 3-26. Piper Diagram Showing Major Ionic Composition for Recharge and Groundwater for Valley Water MAR System in Planning.

3.2.2.5 Truckee Meadows Water Authority

TMWA installed an 8-inch diameter test well to investigate an unconfined coarse alluvial aquifer consisting of unconsolidated sand and gravel extending to 700 fbg and aquifer thickness totaling 550 feet. Aquifer testing yields a transmissivity and storage coefficient of 3,100 ft^2/d and 0.05, respectively. Engineering personnel estimate the aquifer should support recharge capacity of 2 MGD per MAR well. No groundwater chemistry appeared on the utility survey.

3.2.2.6 Water Replenishment District of Southern California

WRD owns the Leo J. Vander Lans Advanced Water Treatment Facility (LVL) in Long Beach, California (Figure 3-20). LVL was constructed to produce advanced treated recycled water for injection into the Alamitos Gap Barrier Project to mitigate seawater intrusion. The Alamitos Gap Barrier Project was originally constructed in 1964 and has undergone numerous expansions. The Los Angeles County Department of Public Works operates and maintains the Alamitos Gap Barrier Project. Currently, recharge used for injection at the barrier consists of approximately a 50/50 blend of imported surface water and treated water from LVL. LVL currently receives tertiary treated recycled water from the Los Angeles County Sanitation Districts' Long Beach Water Reclamation Plant that is treated with MF, RO, and UV/ozone advanced oxidation processes. The facility was commissioned in 2003, with an initial effluent capacity of 3.0 MGD, and was expanded in 2014 to 8.0 MGD, to further offset the use of imported water at the Alamitos Barrier Project.

WRD is currently evaluating an expansion of LVL to produce up to 8 MGD of additional AWT, which would add additional supply to the Alamitos Gap Barrier Project and provide recharge water for future inland injection wells. WRD is installing a pilot injection well at LVL to evaluate and support design of the future inland MAR wells.

3.3 Summary of Survey Geochemical Results

Utilities responding to the project's survey display marked geochemical similarities (Table 3-13). All the participants operate MAR facilities or plan to operate facilities that recharge to sand or sandstone aquifers. Although aquifers composed of carbonate (limestone and dolomite) and vesicular extrusive igneous rocks occur throughout the United States and worldwide, none of the utilities involved in the project employ these types of aquifer for MAR.

All the recharge waters contained near saturated concentrations of DO. Thus, recharge will likely alter redox conditions in the receiving aquifers. Moreover, DO can react directly with reactive metal-bearing minerals in the aquifer that control the chemistry of the migrating recharge by lowering its pH, nitrate, and alkalinity, while increasing concentrations of metals and other constituents including sulfate and carbonate.

Otherwise, recharge consisted of two chemistry types, based on the AWT treatment processes. Recharge treated with membranes displayed low concentrations of TDS, often significantly below 100 mg/L and a sodium—chloride chemistry. In contrast, recharge treated using non-membrane processes displayed more elevated TDS concentrations often exceeding 500 mg/L. Recharge exiting AWT's relying on non-membrane processes produced a range of ionic chemistry including sodium—chloride, mixed cation—bicarbonate and mixed cation—sulfate.

Except for the HRSD and WC's Woodman Point locations, most groundwater displayed concentrations of TDS consistent with fresh water, typically less than 600 mg/L. TDS at HRSD's SWIFT SRC and WC's Woodman Point were in the brackish range ranging between 1,600 and 5,500 mg/L. In addition, groundwater at several of HRSD's SWIFT localities displayed TDS concentrations approaching 25,000 mg/L. Invariably, a utility recharging water under these conditions should condition clay minerals before conducting injection testing or simulating MAR operations with fresh AWT effluent or potable water.

Conversely, Tucson Water and AACo now or will recharge water displaying a higher TDS and ionic strength than the groundwater, however both recharge and groundwater remains in the fresh category. In these situations, newer systems should look closely at the difference in sodium concentrations. High sodium concentrations in the recharge can fragment the edges of clay minerals which initiates migration and eventually brush piling (accumulation) of the fragments.

Several facilities reported geochemical issues during MAR operations involving the appearance of deleterious constituents at nearby monitoring wells. These issues included the following:

- Arsenic mobilization
- Nickel and cobalt mobilization
- Nitrite production
- Elevated TTHM concentrations appearing at monitoring wells

Also, utilities have reported problems related to basin and well clogging through mechanical (siltation), biological (biofouling), and minerals precipitation mechanisms. Basin operators typically handle clogging by annual maintenance including surface ripping (i.e., mechanically breaking up the hard pan) and occasional sediment removal. By comparison, wells create greater complexity regarding maintenance. OCWD, the oldest and largest operator of MAR wells, has developed several innovative yet uniform techniques for maintaining their large network of wells.

Chapter 4 and Appendix C discuss clogging and geochemical issues at MAR facilities in greater detail. Both sections describe applying the project's DFT to these issues to test the validity and effectiveness of the tool in developing solutions for common MAR problems.

Table 3-13. Summary of Utility Survey Geochemical Results.

						Geochemistry											
						Recharge						Groundwater					
Utility	**Location**	**Phase of Operation**	**Predominant Treatment Process**	**Recharge Facilities**	**Aquifer Lithology**	**pH (std units)**	**TDS (mg/L)**	**Ionic strength (m/L)**	**Ionic chemistry**	**Redox category**	**Primary Redox process**	**pH (std units)**	**TDS (mg/L)**	**Ionic strength (m/L)**	**Ionic chemistry**	**Redox category**	**Primary Redox process**
Water Corporation	Perth, Australia	Operating	Membranes, UV, Recarbonation, monochloramine	Wells	Jurassic and Cretaceous - Age Sandstone	7.2	25	6.3E-04	Sodium - Chloride	Oxic	Oxygen reduction	7	191 to 510	4.8E-5 to 1.3E-2	Sodium - Bicarbonate	Anoxic	Iron reduction
Water Corporation	Munster, Australia	Planning	RO and Carbon-Based treatment under consideration	Wells	Jurassic and Cretaceous - Age Sandstone	7.2	25	6.3E-04	Sodium - Chloride	Oxic	Oxygen reduction	7.2 to 7.6	1,600 to 2,100	4.0E-2 to 5.3E-2	Sodium - Chloride	Anoxic	Iron reduction
Tri-Valley Agencies	Livermore-Amador Valley, California	Planning	Several process under consideration	Basins & Wells	Holocene Age Alluvial Sand	7.8	580	1.5E-02	Sodium - Mixed anion	Oxic	Oxygen reduction	7.7	500	1.3E-02	Mixed Cation, Magnesium - Bicarbonate	Oxic	Oxygen reduction
Hampton Roads Sanitation District	Virginia Beach, Virginia	Operating Research Facility	Floc-Sed, Ozone, BAC, GAC UV	Wells	Cretaceous-Age Sand	7.6	660	1.7E-02	Sodium - Chloride	Oxic	Oxygen reduction	7.2	5500	1.4E-01	Sodium - Chloride	Anoxic	Iron reducing
Anne Arundel County, Maryland	Annapolis, Maryland	Planning	Floc-Sed, Ozone, BAC, GAC UV	Well	Cretaceous-Age Sand	8	230	5.8E-03	Sodium - Mixed anion	Oxic	Oxygen reduction	4.5 to 6.1	17 to 35	4.0E-4 to 9.0E-4	Mixed Cation - Sulfate	Anoxic	Nitrate to Iron reduction
Orange County Water District	Fountain Valley, California	Operating	MF, RO, UV, & H_2O_2 addition for advanced oxidation	Basins & Wells	Pliocene to Quaternary Age Alluvial Sand	8.5	49	1.2E-03	Mixed cation - Bicarbonate	Oxic	Oxygen reduction	8	202 to 640	5.1E-3 to 1.6E-2	Calcium - Bicarbonate	Oxic and Anoxic	Oxygen and Methane reduction
Tucson Water	Tucson, Arizona	Operating	Raw surface water	Basins	Alluvial Sand and Gravel	8.4	590	1.5E-02	Mixed cation - Sulfate	Oxic	Oxygen reduction	8	200	5.0E-03	Calcium - Mixed Anion	Anoxic	Nitrate reduction
Valley Water	Campbell, California	Planning	Membranes, UV, Recarbonation, monochloramine	Basins	Quaternary-Age Alluvial Sand	8	100	2.5E-03	Sodium - Chloride	Oxic	Oxygen reduction	7.6	410	1.0E-02	Calcium - Bicarbonate	Anoxic	Iron reduction

Floc-sed - flocculation sedimentation
GAC - granular activated carbon
H_2O_2 - Hydrogen peroxide for advanced oxidation
MF - microfiltration
RO - Reverse osmosis
UV - ultraviolet disinfection
H_2O_2 - Hydrogen peroxide for advanced oxidation

CHAPTER 4

Framework Development

Utilities can employ many approaches in evaluating potential physical and geochemical issues anticipated when applying potable reuse for MAR to basins or wells. Most utilities apply a phased approach organizing MAR projects into the following:

- Phase 1 Geochemical Compatibility Investigation for MAR Projects
- Phase 2 Geochemical Field Investigation
- Phase 3 MAR Facility Start Up and Operations from Geochemical Perspective

The Decision Framework hinges on the three project phases portrayed in primary flowcharts (Figures 4-1 through 4-3) comprising easy to follow pathways. Phase 1 encompasses a fatal flaws analysis that employs data available from the utilities files or literature sources to determine the viability of MAR in an area, site, or specific aquifer(s). The pathways often terminate at nodes that refer the user to secondary flowcharts (Figures 4-4 through 4-10) or salient literature addressing specific geochemical or well/basin clogging issues. Most of secondary charts offer the user several pathways to a solution (Figures 4-6, 4-7, and 4-8), while others describe a restrictive path to solving an issue (Figure 4-5).

4.1 Introduction

A Phase 1 Geochemical Compatibility Investigation MAR Projects (Phase 1) involves a study aimed at seeking critical problems that may render a potential MAR project infeasible. In this section, fatal flaws may entail geochemical reactions that appear too difficult to manage through in situ techniques or any number of other problems involving geochemistry or well/basin clogging or permutations thereof that can combine to render a project infeasible. Just as important, other Phase 1 activities include selecting the receiving aquifer(s), estimating the injection capacities of basins and wells, identifying recharge and groundwater quality characteristics.

Phase 1 studies usually rely on existing data from multiple sources along with rudimentary field activities, if necessary. Thus, Phase 1 studies do not typically require extensive drilling, sampling or testing, however, if no fatal flaws emerge, the study uncovers data gaps that a field investigation can address during a Phase 2 Field Investigation (Phase 2).

A Phase 2 investigation entails conducting a field investigation that characterizes the geologic, hydrogeologic, and geochemical characteristics of the storage aquifer. The process nearly always comprises but does not limit the investigation to the following activities:

- Collecting formation samples in the form of core or drill cuttings
- Obtaining mineralogical analysis of the formation samples
- Performing bore- and surface geophysical surveys
- Conducting batch or bench-scale tests with formation samples and recharge water (recharge)

- Drilling, installing, and developing test and observation wells
- Conducting pumping tests including step drawdown and constant rate tests
- Conducting injection tests
- Collecting water quality samples of groundwater and recharge, if available

By completing the type of Phase 2 investigation outlined above the utility can build a strong understanding of geologic, hydrologic, and geochemical characteristics of the test site. Moreover, testing during the field investigation enables developing design criteria for constructing a permanent MAR facility including recharge wells and basins, AWT needs, monitoring systems, aquifer conditioning, etc., for implementation during Phase 3.

Phase 3 MAR Operations (Phase 3) usually consists of designing, permitting, constructing the MAR facility and ultimately operating the facility, and thus represents, by far the phase lasting the longest. Fortunately, identification of most physical and geochemical issues that can affect MAR operations occur during Phases 1 and 2. Still, several issues remain unresolved into Phase 3 particularly if construction of the AWT happens coincident with Phase 3 activities. Thus, although simulated recharge quality can support simulating geochemical reactions, the most accurate simulations originate from actual recharge chemistry. Just as important, operators cannot evaluate the clogging potential of the recharge before commissioning the AWT.

Chapter 4 discusses the framework of a potable reuse MAR project and how a utility can identify important clogging or geochemical reactions during each project phase. Chapter 4 describes how to navigate the contents of the Excel-based DFT, developed to guide utilities through issues related to undesired geochemical reactions and basin/well clogging. Appendix D contains information on the approach and methodology used in the DFT.

4.2 Chapter 4 Objectives

The objectives of Chapter 4 include:

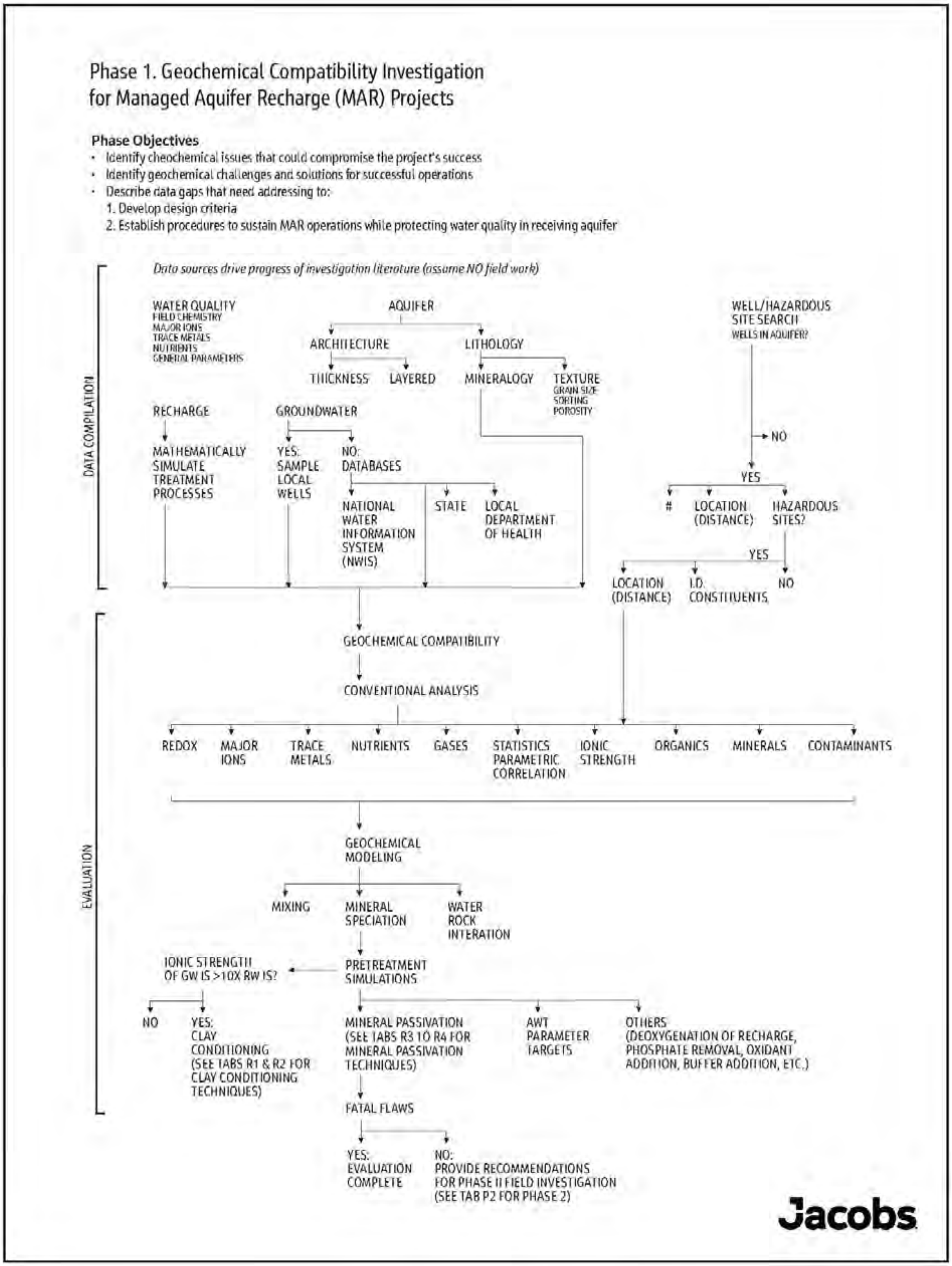
- Guiding utilities in selecting the best aquifer(s) for MAR operations from a geochemical perspective.
- Assessing the geochemical compatibility between recharge, groundwater, and aquifer mineralogy and amorphous phases.
- Determining the need for aquifer conditioning prior to starting MAR operations.
- Resolving whether recharge water requires pretreatment to passivate potential deleterious reactions in situ.
- Selecting the best pretreatment measures depending on recharge chemistry and aquifer mineralogy.
- Long-term well performance monitoring.
- Long-term monitoring of recharge migrating in the aquifer.

The section steps the user through the MAR Project Phases (Figures 4-1, 4-2, and 4-3) while discussing which phases identify the important geochemical reactions and clogging issues. Project phases form the essential baseline for branching off into geochemical reactions. Accordingly, Project Phases 1 through 3 form the basis for sections in Chapter 4.

4.3 Phase 1—Identifying Fatal Flaws

From a geochemical perspective, a Phase 1 analysis (elsewhere described as a MAR Feasibility Investigation, Feasibility Study, Entry Level Assessment, or fatal flaws analysis) entails identifying conditions or reactions during MAR operations that render developing a MAR facility at a specific location, region, or aquifer inviable. Typically, a Phase 1 involves minimal field investigation work. Instead, a Phase 1 Study relies on compiling water and aquifer chemistry data from existing wells, online databases (Figure 4-1), literature, and utility records.

A Phase 1 can also entail groundwater flow modeling to investigate recharge well capacities, potentiometric levels in the aquifer, and effects of hydraulic interference between basins, wells, and local users. Many studies focus on travel times through the aquifer between the MAR facility and local users. Because of the relative scarcity of data, during the usual Phase 1 the modeling typically entails rudimentary analytical groundwater flow models combined with semi-analytical particle-tracking. However, the data collected in some areas during previous studies support developing or modifying more sophisticated numerical groundwater flow and solute transport modeling.



Phase 1. Geochemical Compatibility Investigation for Managed Aquifer Recharge (MAR) Projects

Phase Objectives
- Identify cheochemical issues that could compromise the project's success
- Identify geochemical challenges and solutions for successful operations
- Describe data gaps that need addressing to:
  1. Develop design criteria
  2. Establish procedures to sustain MAR operations while protecting water quality in receiving aquifer

Figure 4-1. Decision Framework Flowchart for Phase 1 Analysis.

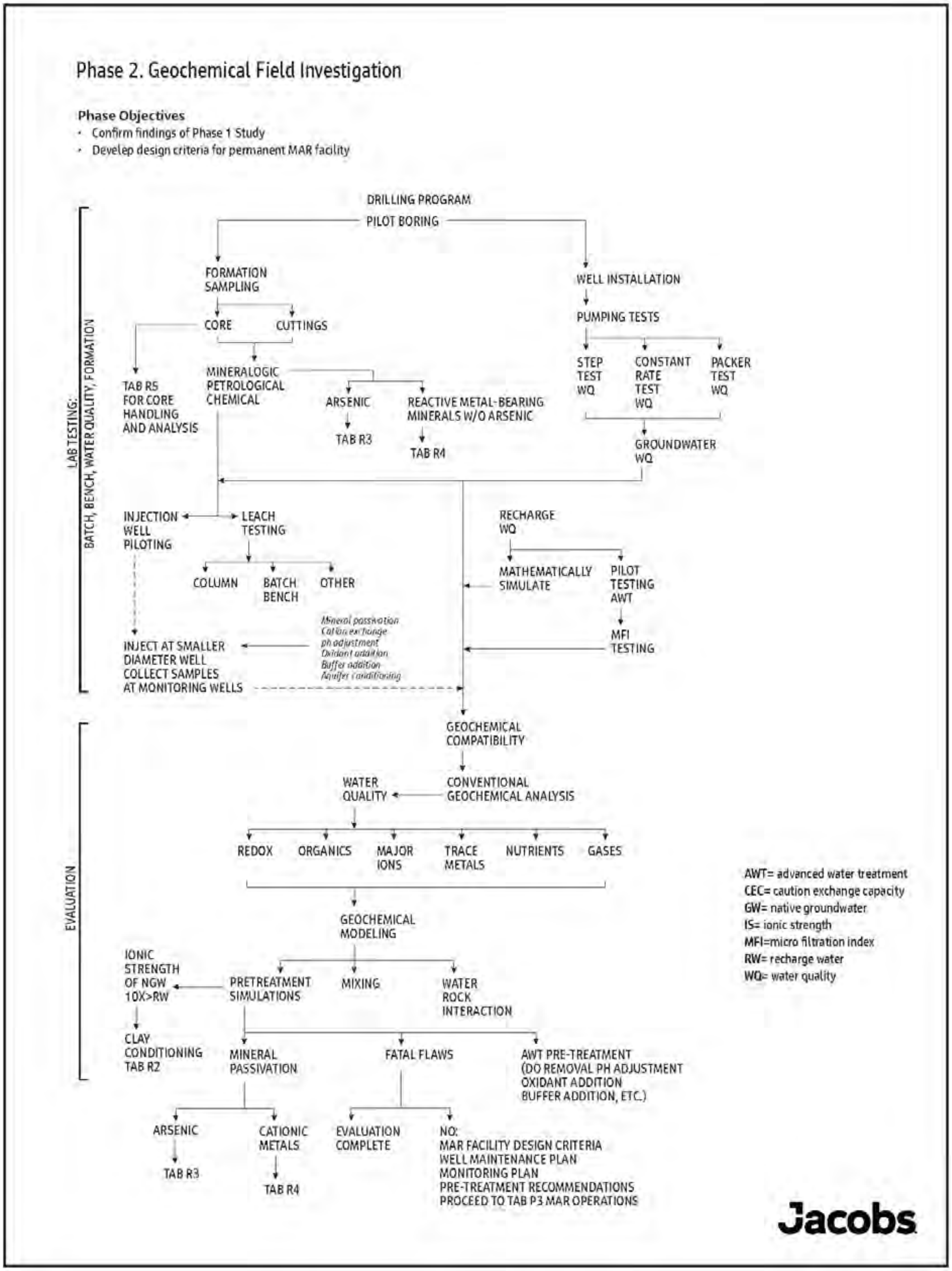
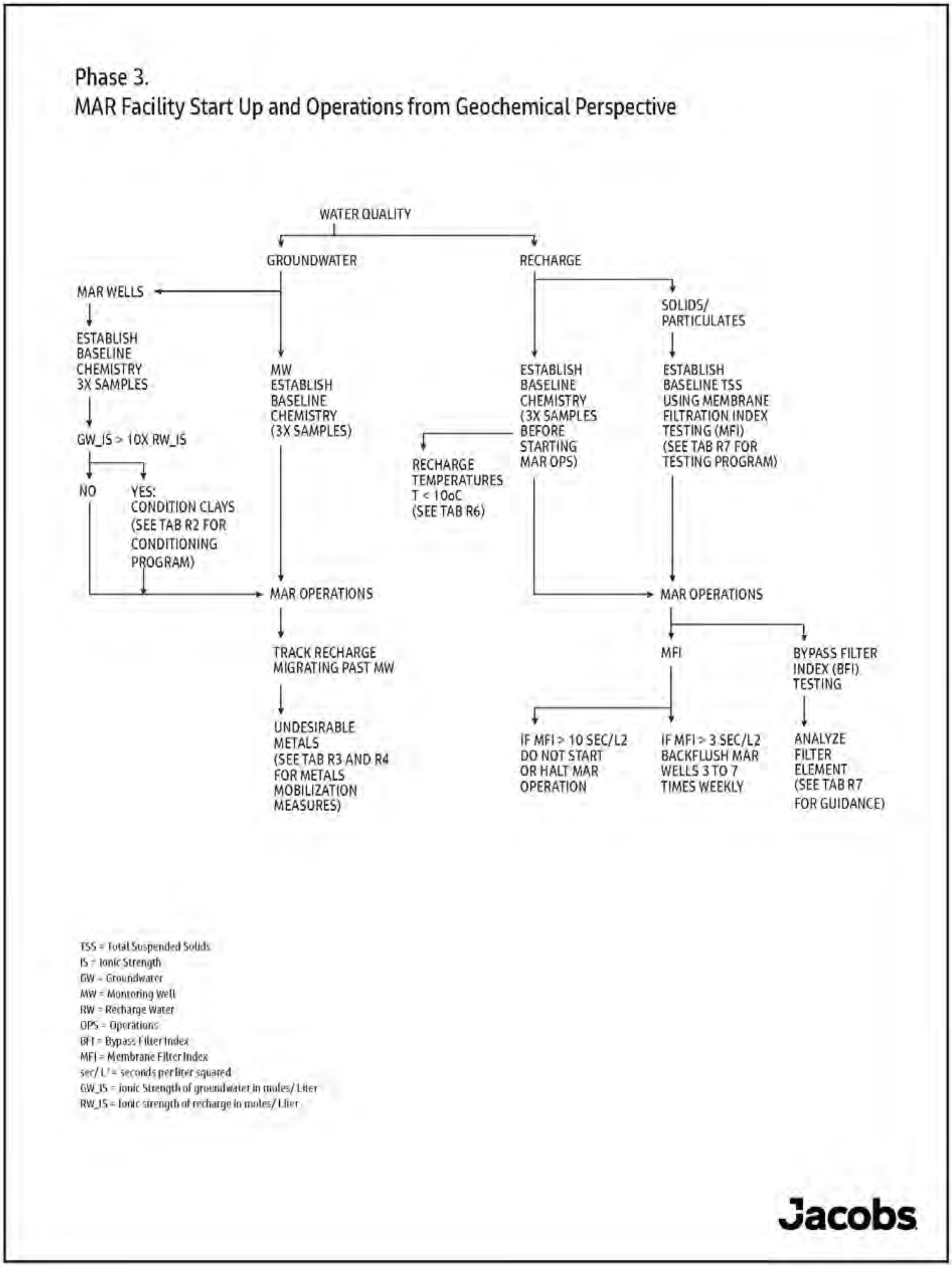


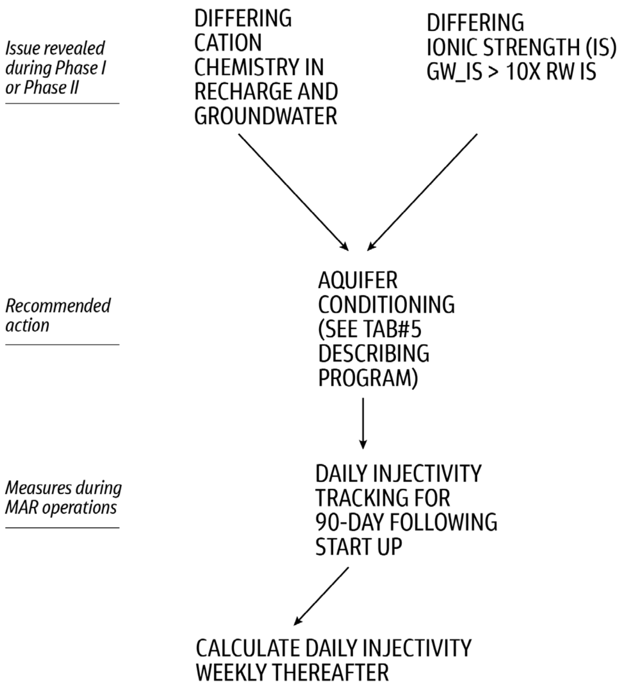
Figure 4-2. Decision Framework Flowchart for Phase 2 Field Investigation.



Phase 3.
MAR Facility Start Up and Operations from Geochemical Perspective

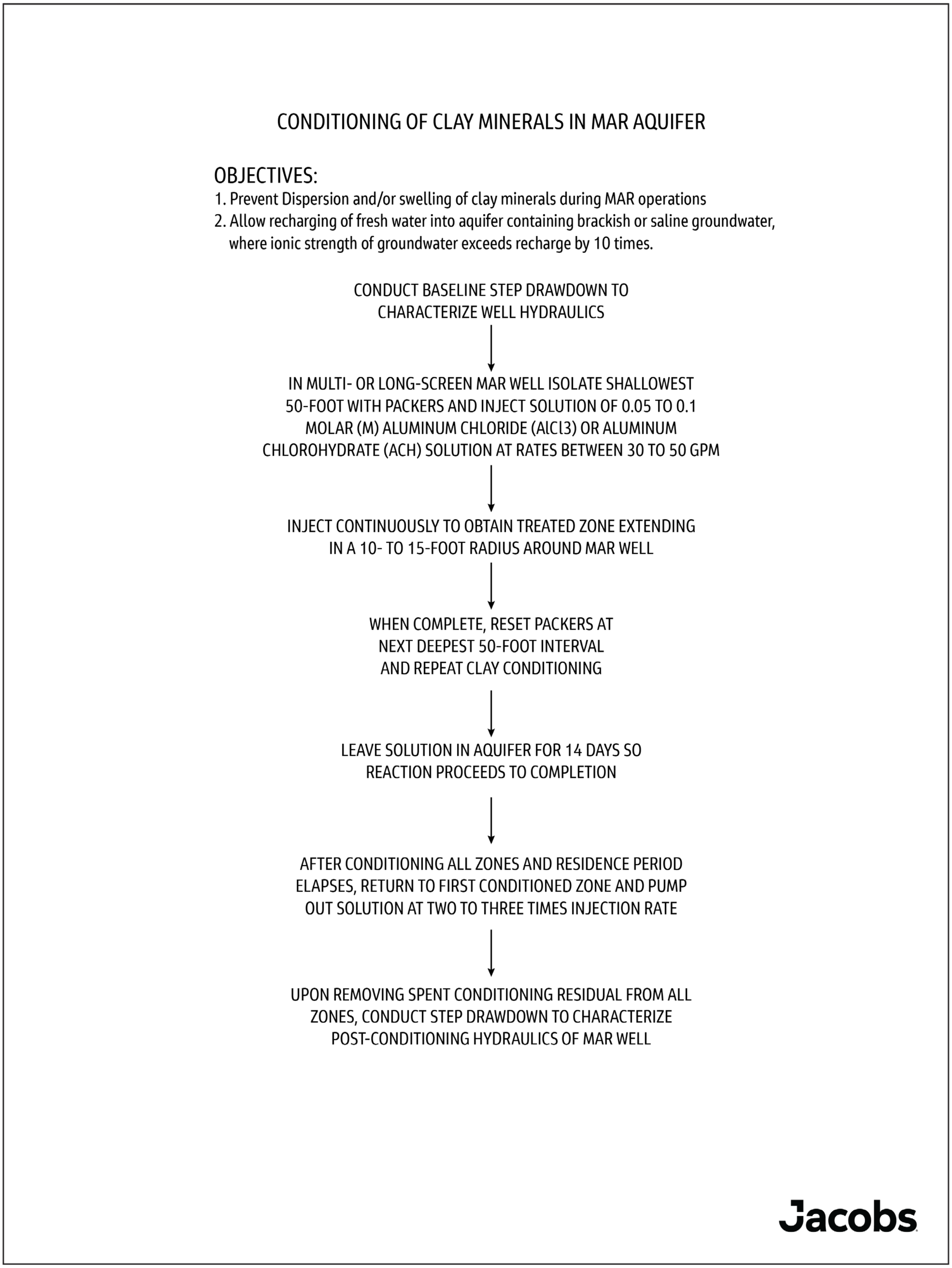
TSS = Total Suspended Solids
IS = Ionic Strength
GW = Groundwater
MW = Monitoring Well
RW = Recharge Water
OPS = Operations
BFI = Bypass Filter Index
MFI = Membrane Filter Index
sec/ L^2 = seconds per liter squared
GW_IS = ionic Strength of groundwater in moles/ Liter
RW_IS = Ionic strength of recharge in moles/ Liter

Figure 4-3. Decision Framework Flowchart for Phase 3 MAR Startup and Operations.



Jacobs.

Figure 4-4. Flowchart for Ionic Strength.



CONDITIONING OF CLAY MINERALS IN MAR AQUIFER

OBJECTIVES:

1. Prevent Dispersion and/or swelling of clay minerals during MAR operations
2. Allow recharging of fresh water into aquifer containing brackish or saline groundwater, where ionic strength of groundwater exceeds recharge by 10 times.

CONDUCT BASELINE STEP DRAWDOWN TO CHARACTERIZE WELL HYDRAULICS

↓

IN MULTI- OR LONG-SCREEN MAR WELL ISOLATE SHALLOWEST 50-FOOT WITH PACKERS AND INJECT SOLUTION OF 0.05 TO 0.1 MOLAR (M) ALUMINUM CHLORIDE (AlCl3) OR ALUMINUM CHLOROHYDRATE (ACH) SOLUTION AT RATES BETWEEN 30 TO 50 GPM

↓

INJECT CONTINUOUSLY TO OBTAIN TREATED ZONE EXTENDING IN A 10- TO 15-FOOT RADIUS AROUND MAR WELL

↓

WHEN COMPLETE, RESET PACKERS AT NEXT DEEPEST 50-FOOT INTERVAL AND REPEAT CLAY CONDITIONING

↓

LEAVE SOLUTION IN AQUIFER FOR 14 DAYS SO REACTION PROCEEDS TO COMPLETION

↓

AFTER CONDITIONING ALL ZONES AND RESIDENCE PERIOD ELAPSES, RETURN TO FIRST CONDITIONED ZONE AND PUMP OUT SOLUTION AT TWO TO THREE TIMES INJECTION RATE

↓

UPON REMOVING SPENT CONDITIONING RESIDUAL FROM ALL ZONES, CONDUCT STEP DRAWDOWN TO CHARACTERIZE POST-CONDITIONING HYDRAULICS OF MAR WELL

Figure 4-5. Clay Conditioning.

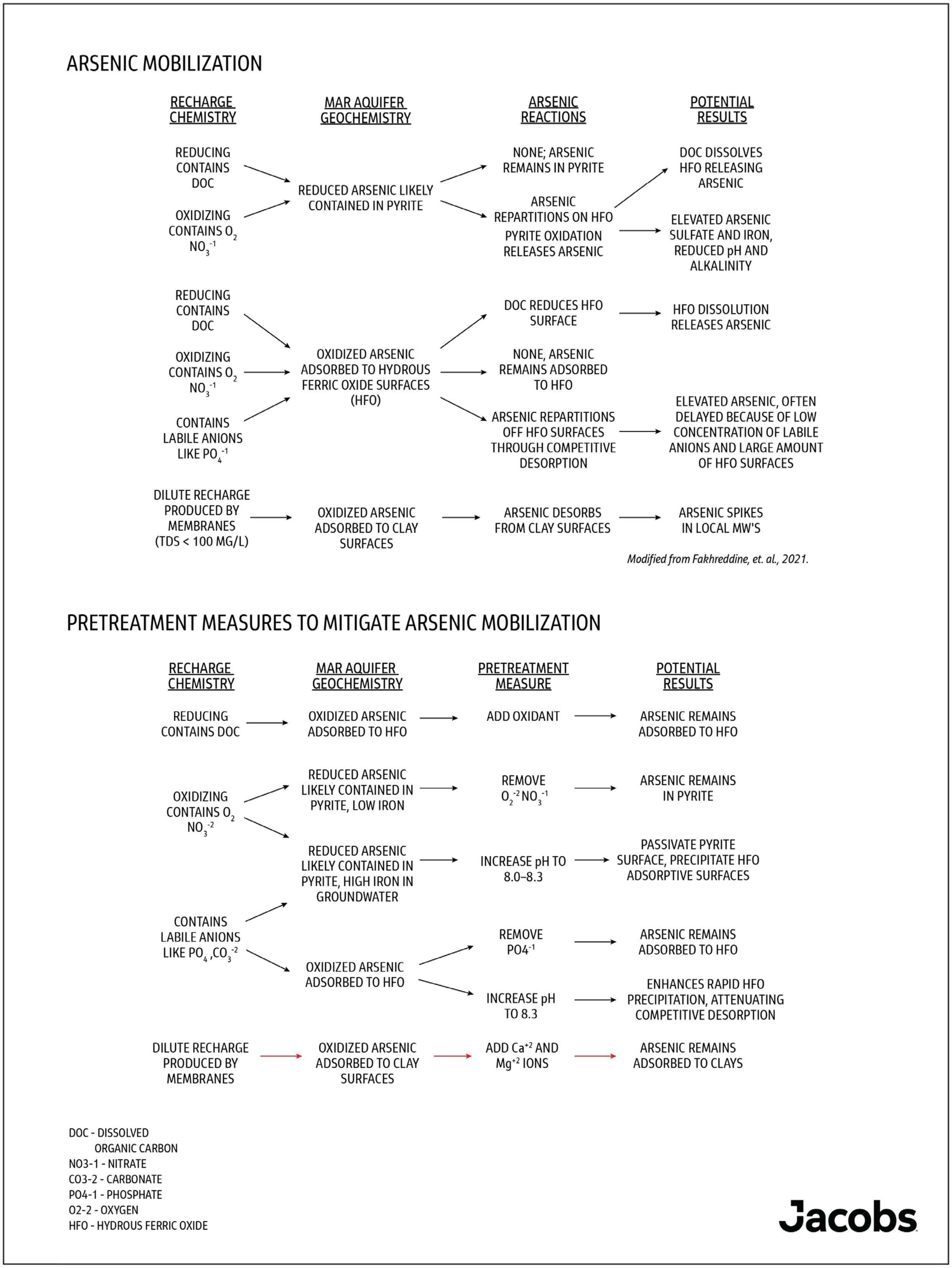


Figure 4-6. Decision Framework Flowchart showing Arsenic Mitigation.

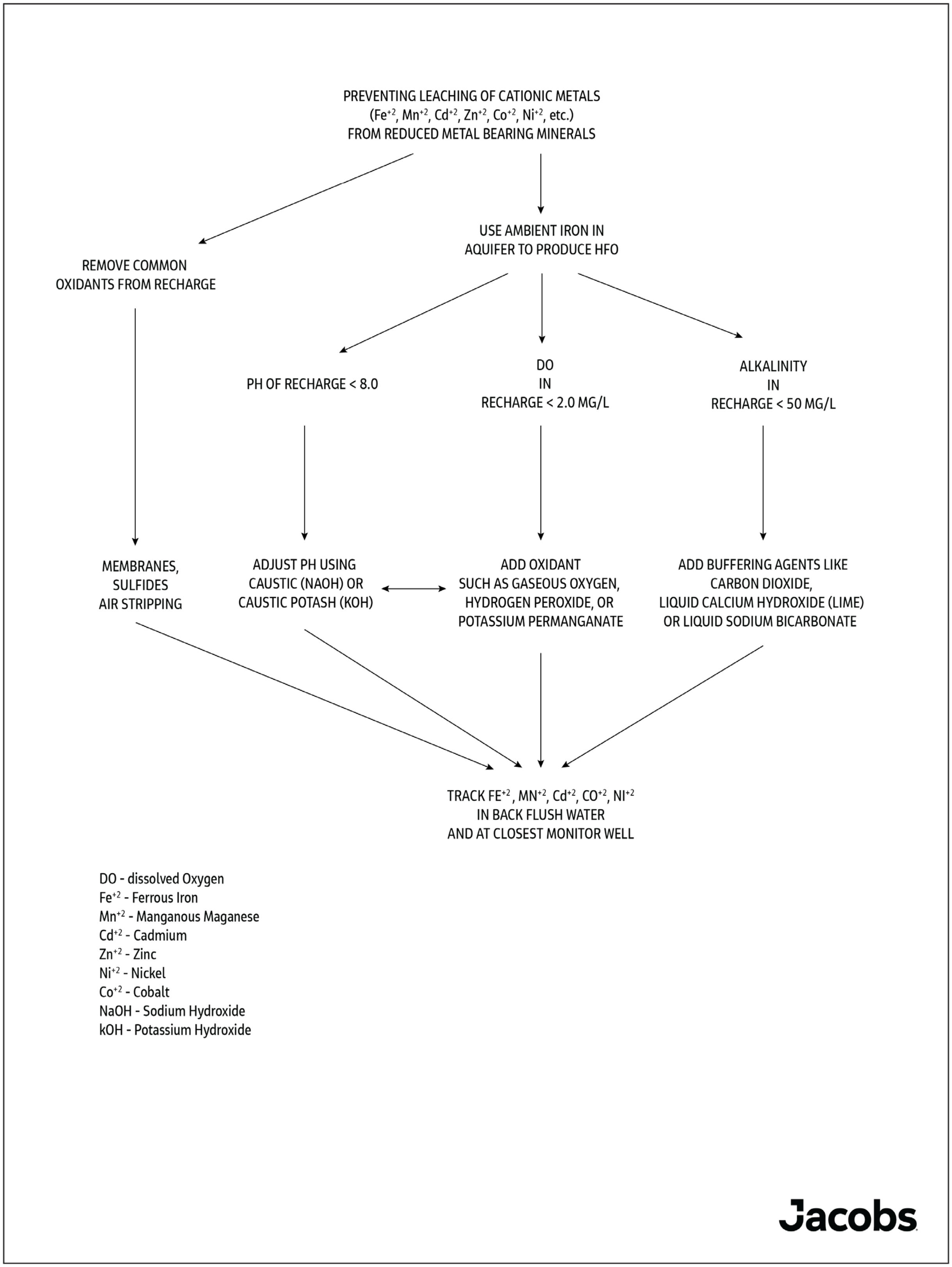


Figure 4-7. Decision Framework Flowchart for Mitigating Cationic Metals.

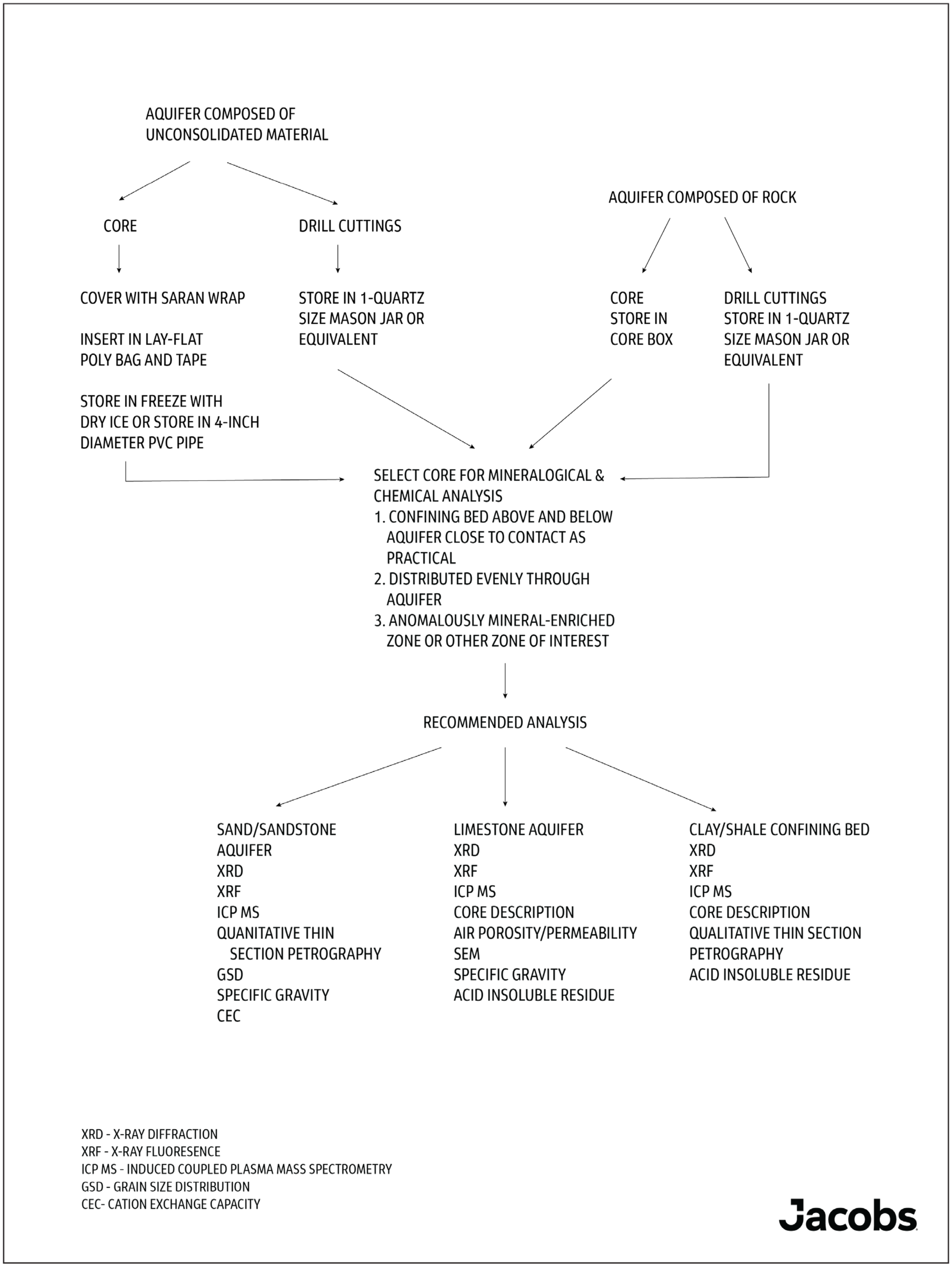


Figure 4-8. Formation Sampling for Mineralogic and Chemical Analysis.

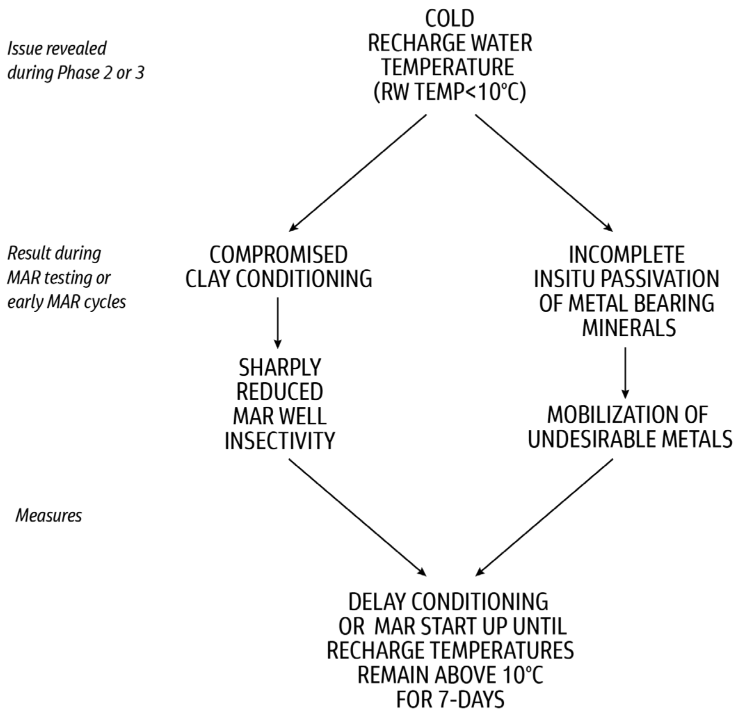


Figure 4-9. Flowchart Involving Cold Recharge Water.

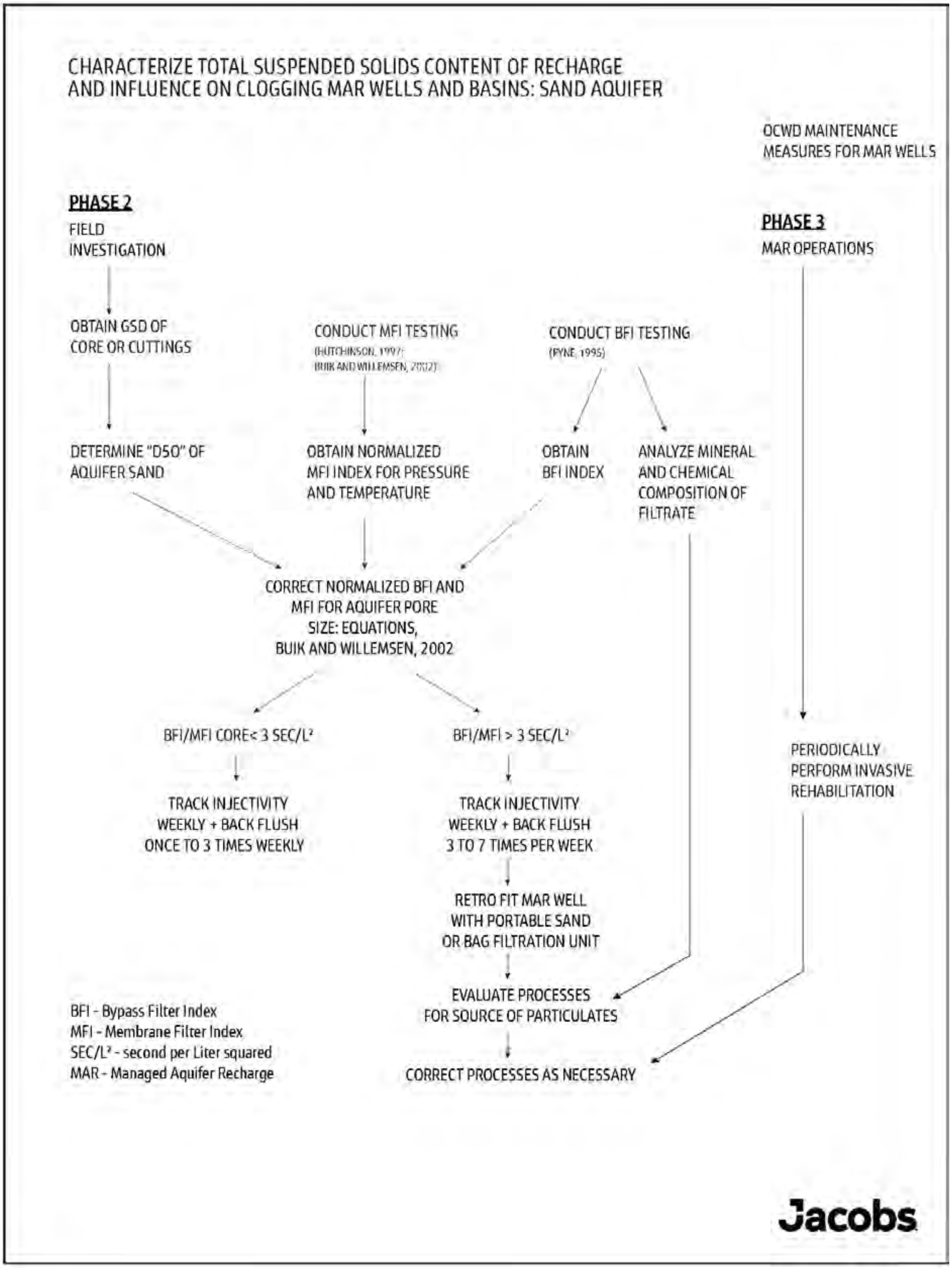


Figure 4-10. Decision Framework Flowchart for MFI Testing.

Occasionally, local wells installed in the aquifer under consideration for the project may prove accessible for sampling. Yet, more often the project personnel obtain groundwater chemistry from existing sources. Only in rare situations does a utility have recharge water chemistry available from an AWT facility available for evaluation. Yet, by knowing the planned treatment processes, engineers can mathematically simulate accurate water quality analyses containing pH, oxidation-reduction potential, major ions, trace metals, nutrients, and general water quality parameters as illustrated in Table 4-1. Conversely, the clogging potential of recharge remains unknown until later phases of the project, usually not until piloting or constructing the AWT.

Table 4-1. Summary of Recommended Field and Laboratory Analytes.

Field Chemistry	Measurement Units	MDL
pH	standard units	0.1
ORP	mv	50
Specific Conductivity	µS/cm	10
Dissolved Oxygen	mg/L	0.01
Temperature	ºC	0.1
Turbidity	NTU	0.1
Field Sulfate	mg/L	5
Field Iron (ferrous)	mg/L	0.01
Field Iron (total)	mg/L	0.01
Field Manganese	mg/L	0.01
Field Sulfide	mg/L	0.01
Chloride	mg/L	10
Alkalinity	mg/L	20
Carbon dioxide	mg/L	1
Laboratory Analytes		
Aluminum dissolved	mg/L	0.01
Aluminum total	mg/L	0.01
Arsenic dissolved	mg/L	0.0001
Arsenic total	mg/L	0.0001
Iron dissolved	mg/L	0.01
Iron total	mg/L	0.01
Manganese dissolved	mg/L	0.005
Manganese total	mg/L	0.005
Calcium total	mg/L	1
Potassium total	mg/L	1
Magnesium total	mg/L	1
Sodium total	mg/L	1
Sulfate	mg/L	1
Alkalinity	mg/L	10
Chloride	mg/L	1
Sulfide	mg/L	0.01

Field Chemistry	Measurement Units	MDL
Nitrate as N	mg/L	0.01
Nitrite as N	mg/L	0.01
Total Kjeldahl Nitrogen	mg/L	0.1
Fluoride	mg/L	0.01
Silica	mg/L	1
Total organic carbon	mg/L	0.5
Dissolved organic carbon	mg/L	0.5
Total phosphorus	mg/L	0.1
Orthophosphate	mg/L	0.1
Total dissolved solids	mg/L	10
Total suspended solids	mg/L	0.5
Hardness	mg/L	10
Ammonia	mg/L	0.1
Total THMs	µg/L	1
Chloroform	µg/L	1
Bromoform	µg/L	1
Bromodichloromethane	µg/L	1
Dibromochloromethane	µg/L	1
Total HAA	µg/L	1
Gross Alpha	pCi/L	1
Radium 226	pCi/L	1
Radium 228	pCi/L	1
Uranium	mg/L	0.1

The above list contains enough analytes for a thorough analysis, yet recognizes operator may need to customize the analytes to issues as they arise.

MDL = recommended method detection limit
NTU = nephelometric turbidity unit

Geochemically, a Phase 1 should involve the follow data gathering activities:

- Mathematically simulating AWT effluent.
- Compiling groundwater chemistry from literature and databases like the USGS's National Water Information System, or state and county systems.
- Obtaining aquifer information including hydraulic coefficients, lithology, texture, and mineralogy from USGS and state survey reports.
- Conduct a search to identify local production and/or monitoring wells and hazardous sites using state or commercial services.

Geochemically, aquifer information should focus on the unit's thickness, architecture (single or multiple layers), lithology, and mineralogy. Except for the occasional petrographic study, most reports describe lithology and mineralogy in the most general terms and thus, hold minimal value for the Phase 1 Study evaluation. To the extent practical, water chemistry gleaned from report database sources should contain a comprehensive list of analytes and include source locations along with the date of sampling. Every Phase 1 should involve a local well and hazardous site search. At many prospective sites, local industrial and commercial activities have released hazardous chemicals into the groundwater system presenting water quality and regulatory issues for the site under consideration.

At MAR facilities, recharging water to the water table through basins or dry wells elevating water levels can potentially liberate contaminants trapped in the vadose zone. In confined aquifers, elevated potentiometric levels could alter the migration direction of contaminant plumes. Conversely, MAR facilities if strategically located can protect existing water supply infrastructure from advancing plumes, forming a hydraulic barrier that blocks the migration of contamination toward a well or wellfield.

Careful review of the available contaminant data, in consideration with the intended recharge mechanism(s) (wells of basins) and the aquifer type (unconfined or confined), are critical to determining if the presence of contamination is a fatal flaw or if recharge could present a potential benefit by protecting regional water quality from additional degradation by preventing contaminant migration.

4.3.1 Conventional Geochemical Analysis

Upon obtaining recharge and groundwater chemistry, the data requires vetting to examine analytical accuracy before committing it to the rigors of evaluation. The vetting process involves examining the cation-anion balance, the relationship between major ions and TDS and specific conductivity, and assessing the accuracy of trace metal, nutrient, and general water quality concentrations. Spreadsheets accommodate determining the cation-anion balance as described by (Stuyfzand 1993):

$IB = 100 X (\Sigma k - \Sigma a(/(\Sigma k + \Sigma a)$

Where:

IB = ionic balance in percent

Σk = sum of cations in Meq/L

Σa = sum of anions in Meq/L

Expressed in milli-equivalents per liter (Meq/L) total cation and anion concentrations should fall within 5 percent of each other. Should the totals vary by greater than 5 percent, the user should discard the data from further use or note the problematic balance when employing the analysis in the evaluation. Sometimes, out-of-balance analyses represent the only data available and thus, the user must, with misgivings incorporate the data in the Phase 1. Conventional geochemical analyses comprise applying statistical, graphing, and plotting techniques using the recharge and groundwater chemistry, and to the extent practical mineralogy.

- Techniques used in describing predominant ionic species and the relationship between samples will involve:
  1. Diagrams
  2. Stiff Diagrams
  3. Cation ratios

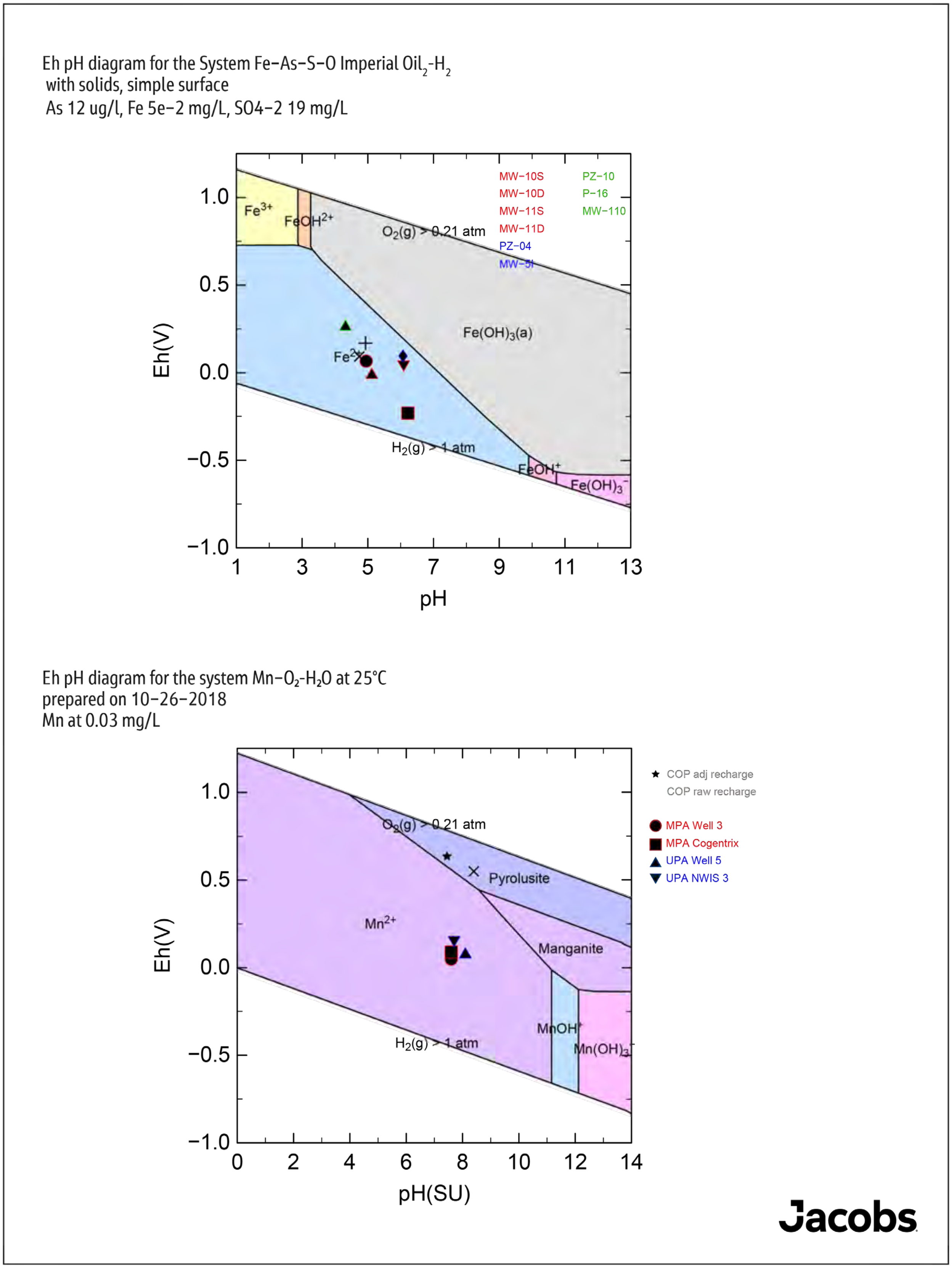
- Analysis of the redox potential of water samples will comprise:
  1. Redox diagrams
  2. Redox Constituent Analysis

- Assessing the stability of clays and metal-bearing minerals (iron, manganese, aluminum, arsenic, etc.) in the receiving aquifer(s) will employ the following techniques:
  1. Parametric statistics
  2. Correlation Coefficients
  3. Regression Analysis
  4. Predominance Area Diagrams
  5. Phase Diagrams

Piper and Stiff diagrams plot cation and anion equivalent concentrations either as percentages (Piper) or absolute values (Stiff), to graphically display the predominant ionic species and the relationship between samples.

Redox line diagrams and the Jurgens et al. (2009) redox constituent analysis help describe redox conditions in the aquifer based on aqueous analysis. These techniques become particularly important when considering (for example) the mobility of metals in the receiving aquifer(s) under changing redox conditions caused by an oxygen-rich recharge water. Under the circumneutral pH conditions found in most aquifers, redox potential controls the mobility of iron, manganese, and arsenic, and the characteristics of adsorptive mineral surfaces that can hinder their mobility.

Phase diagrams provide a powerful tool for assessing aqueous and mineral equilibria during Phase 1 studies (Figure 4-11). The diagrams facilitate plotting the path traversed between dissolved ions and minerals during storage in an aquifer. The programs PHREEPLOT (Kinniburgh and Cooper 2011), The Geochemist's Workbench, (Aqueous Solutions LLC 2021) and Hydra-Medusa (Puigdomenech 2009) enable preparing various types of predominance area and phase diagrams. Users can obtain PHREEPLOT and Hydra-Medusa for free online, while obtaining the Geochemist's Workbench requires purchasing a license. PHREEPLOT, linked to the geochemical model software PHREEQC (Parkhurst 1995), developed by the USGS, provides enormous flexibility for handling complex geochemical environments.



Eh pH diagram for the System Fe–As–S–O Imperial Oil$_2$-H$_2$ with solids, simple surface As 12 ug/l, Fe 5e–2 mg/L, SO4–2 19 mg/L

Eh pH diagram for the system Mn–O$_2$-H$_2$O at 25°C prepared on 10–26–2018 Mn at 0.03 mg/L

Figure 4-11. Examples of Iron and Manganese—Oxide—Water Phase Diagrams.

4.3.2 Geochemical Modeling

Utilities will typically use geochemical models during every phase of a MAR project. During a Phase 1 models have proven particularly useful in simulating the following reactions and chemical relationships:

- Reactions between recharge water, native groundwater, and aquifer mineralogy.
- Aquifer conditioning techniques to stabilize minerals or amorphous phases in situ.
- Long-term changes in the redox, acid-base, clay chemistry, etc. environment during MAR operations.
- Speciating ions and complexes.
- Developing saturation indices for potential mineral phases.
- Calculating ionic strengths of aqueous samples.
- Calculating activities of constituents for plotting phase diagrams.

Geochemical modeling helps identify the potential presence of minerals from a groundwater quality analysis, or not detected in XRD or petrographic analysis conducted during later phases of a MAR project. Many minerals can go undetected because of their lack of crystallinity (amorphous phases), or because lithologic sampling does not cover every depth interval of the aquifer section. Moreover, amorphous minerals often reside in the interstitial spaces of aquifers. Consequently, these phases can display a high degree of reactivity, thus, potentially playing an important role in controlling groundwater or recovered water chemistry.

4.3.2.1 Modeling Software Summary Description

Utilities can employ models available in the public domain like PHREEQC (Parkhurst and Appelo 1999), the Geochemist's Workbench (Aqueous Solutions, Inc. 2021; Bethke 2008), PHREEPLOT, and MINTEQA2 (Allison, et al. 1991) in performing geochemical modeling simulations. The USGS model, PHREEQC utilizes extensive thermodynamic databases to perform speciation and mineral phase calculations for user-entered water chemistry data. These calculations are useful in describing the geochemistry and estimating the mineralogy that influences the water quality. During injection testing, PHREEQC performs many functions for evaluating the interactions between recharge, groundwater, and the receiving aquifer, including transport, mixing, cation exchange, surface complexation, simple chemical reactions, speciation, and inverse modeling.

MINTEQA2 was developed by the EPA to perform equilibrium calculations on metals contaminating groundwater at Resource Conservation and Recovery Act and Comprehensive Environmental Response, Compensation, and Liability Act sites. The program does not display the extensive capabilities of PHREEQC but offers several functions useful for evaluating surface complexation of metals in MAR aquifers, including modules supporting cation exchange, and a wide range of surface complexation models (Langmuir, Freundlich, Diffuse Double-Layer, Triple Layer and Constance Capacitance).

Running geochemical models requires some specialized training. A college-level or refresher course in general chemistry and then training on the specific model provides sufficient background to run simulations supporting a Phase 1 investigation using PHREEQC and MINTEQA2. In the United States, the National Groundwater Association offers a two-day course in running PHREEQC including running speciation, mixing, adsorption, kinetics, and other simulations.

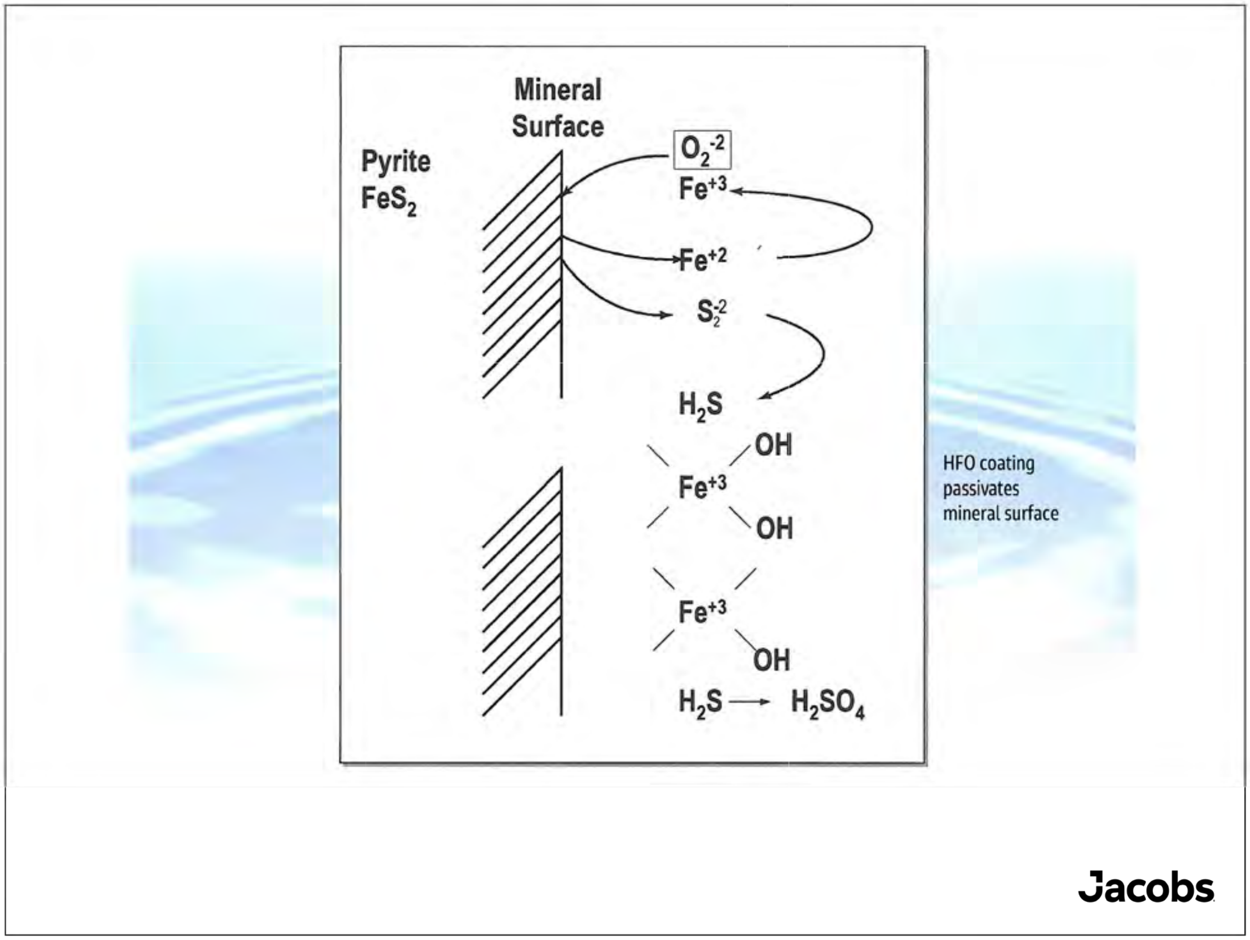
PHREEPLOT (Kinniburgh and Cooper 2011) and Hydra-Medusa (Puigdomenech 2009) use complex algorithms to plot multiple types of equilibrium diagrams. PHREEPLOT runs on the PHREEQC engine and, thus, requires training in using PHREEQC to generate diagrams. Conversely, Hydra-Medusa runs on a menu- and graphics-based platform expediting training and the ease of making diagrams.

4.3.2.2 Modeling Approaches

During Phase 1, the first modeling simulations apply analytical results from simulated recharge and groundwater samples grabbed from databases as input to identify potential minerals or amorphous phases present in the aquifer matrix. Upon revealing minerals in equilibrium with groundwater, Phase 1 modeling simulates mixing between the recharge and groundwater to uncover reactions that may migrate with the leading edge of recharge plume. The modeler can introduce minerals encountered during the initial modeling into mixing simulations.

Similarly, modeling involves reacting minerals identified in the aquifer samples with constituents in the recharge water like DO, nitrate, dissolved iron, and others. The simulations help characterize the mobility of common trace metals in the receiving aquifer during MAR operations. By identifying the metals that are more likely to mobilize through modeling, the analyst can test the effectiveness of pretreatment schemes in stabilizing the metals in situ (Figure 4-12).

At present models cannot accurately simulate dispersing clays during MAR operations, however they can identify differences in ionic strength between recharge and groundwater and evaluate cation exchange. Also, the models allow accurately simulating the conditioning of clay minerals using aluminum, calcium, or potassium salts (Al-, Ca-, or K-salts).



HFO coating passivates mineral surface

Figure 4-12. Conceptual Depiction of Pyrite Oxidation.

Although the Phase 1 represents a relatively cursory evaluation of geochemical conditions, in addition to uncovering fatal flaws, a utility can make important decisions regarding the permanent facility and augment processes at the AWT. As shown on the Phase 1 project framework (Figure 4-1), a utility can determine the following:

- Whether anthropogenic contaminants represent a potential issue
- The ionic strength of recharge and groundwater (Figure 4-4).
- If the ionic strength of groundwater exceeds the recharge by 10 times, the aquifer will likely need conditioning with Al-, Ca-, or K-salts to preclude dispersing clays during MAR (Figure 4-5).
- Potential cation exchange reactions.
- Potential reactive minerals and amorphous phases in equilibrium with groundwater (Figures 4-6 and 4-7).
- Model pretreatment schemes including chemical and dosages for reducing the reactivity of minerals (passivate), like adjusting pH, adding an oxidant, adding a buffering agent, etc.
- Develop pH and alkalinity targets for the recharge that ensure creating favorable reactions in the aquifer during MAR while preventing the precipitation or dissolution reactions that might reduce aquifer permeability or create regulatory issues, respectively.

- The potential for competitive adsorption when the recharge contains oxy-anion like phosphate or carbonate.
- The probability of acid-base reactions during pyrite or other sulfide mineral oxidation.

The flowchart developed for a Phase 1 directs the user to other materials, literature, and potential solutions to common geochemical reactions during MAR. These reactions involve:

- Differing ionic strength.
- Conditioning of aquifer clays.
- Handling metal mobilization.
- Passivating cationic metals in the absence of arsenic.
- Elevated TOC in recharge water.
- Operational measures with cold recharge (Figure 4-9).
- A portal to the Phase 2 Field Investigation.

4.4 Phase 2—Comprehensive MAR Evaluation

The Phase 2 describes the field investigation developed during Phase 1 to advance the MAR project toward designing a full-scale MAR facility. Phase 2 provides site-specific data to confirm or refute assumptions from Phase 1 while covering data gaps identified during Phase 1. The Phase 2 will entail drilling, installing, developing, and testing a test well to obtain aquifer hydraulic characteristics while enabling a large range of testing. Several factors can dictate the number of test wells required including number and proximity of sites, aquifers, and depth of section. The field effort will involve sampling aquifer materials, groundwater quality, potentially recharge, along with extensive analysis of the samples including mineralogic, elemental, water quality analysis, and various types of bench, batch, leaching or column testing (Figure 4-2).

A Phase 2 program might also entail conducting injection testing at a test well or basin, usually smaller in size than an operational MAR well/basin. Although Phase 2 advances project knowledge significantly, in the absence of an AWT or AWT pilot testing, as mentioned previously, often actual recharge chemistry remains unavailable. So, if the utility conducts injection testing, operators use potable water or prepares a solution using potable water or synthetic recharge created by adding analytes to potable water so that the chemistry resembles the future recharge water.

4.4.1 Test Drilling and Sampling

Initial field activities involve collecting formation samples from a test boring in the form of core or drill cuttings. Core samples provide the most representative samples from the aquifer. The newest wire-line coring techniques allow advancing the borehole by drilling or coring, rather than continuous coring inherent with older systems. Using a wire-line to extract the core from the bit better protects the core from damage, preserves fine content, and precludes oxidation of the core compared to older systems reliant on removing drilling pipe.

However, coring consumes time to obtain samples and added personnel to handle, store, and ship selected samples to a laboratory. In unconsolidated formations, core recovery particularly in loose sands can prove difficult. If the material resists entering the core barrel, coring action can grind away much of the sample, leaving investigators with minimal sample for analysis. Moreover, coring costs can approach $500 (USD) per foot, and combined with the necessary labor, coring can exemplify a significant expensive element of a Phase 2.

Given the tendency toward poor recovery in unconsolidated aquifers, the field team is often forced to submit cutting samples for lab analysis in the absence of core or poor core recovery. Furthermore, if the drilling method confidently returns cuttings at the ground surface that accurately represent drilling depths, such as reverse circulation drilling methods, the field team may elect to forgo coring and instead submit cuttings samples for mineralogical analysis.

Given the cost savings from not coring, the team can submit more samples for analysis, obtaining a comprehensive view of aquifer mineralogy. However, drilling fluids can influence the quality of cutting samples, while the winnowing of fines from the sample can under-represent the number of clays and minerals inhabiting the finer-grained portion of the aquifer. This factor can compromise an evaluation of reactive minerals and subsequent pretreatment techniques devised to treat the minerals in situ.

Some coring studies rely on maintaining the sample in its ambient redox state. Thus, investigators may employ leucite sleeves, customized glove boxes, special canisters, or other techniques for maintaining the anoxic nature of the core. Even without a special requirement regarding anoxic conditions, unconsolidated core requires special preparation for shipment to a lab or long-term storage including:

- Wrapping the core in saran-type plastic wrap and taping the ends and central length of sample to a plastic tray.
- Inserting the tray into a Lay-flat polyethylene bag (poly-bag), stapling the ends, and taping the ends and central length of the core.
- Inserting the wrapped core in a 3- or 4-inch-diameter PVC pipe and placing PVC caps over the ends of the pipe.

During each process, the field team should mark footages, date collected and project information on the wrap, poly-bag and PVC pipe, along with striping each covering material to indicate the direction up. The process does not maintain anoxic conditions like a glove box or nitrogen blanket but will protect the core from oxidation during shipment to a lab or for analysis after longer after longer term storage. Quick-freezing the core using dry ice after wrapping maintain fines and pore water in situ. The process works well with rock core if the field team anticipates extended delays before core analysis. Oxidation on the outer surface of core samples during storage can influence the mineral suite detected during x-ray diffraction or petrographic analysis.

At the completion of drilling, field personnel should prepare a graphical log (Figure 4-13) across the coring interval displaying intervals of no recovery, lithology, mineralogy, bedding characteristics, etc. Several commercially available programs accommodate connecting the lithologic log with well construction, geophysical logs, drilling rates, water quality, and other data collected during drilling. Even in its rudimentary form, the log will help guide project personnel in selecting samples for shipment to a lab.

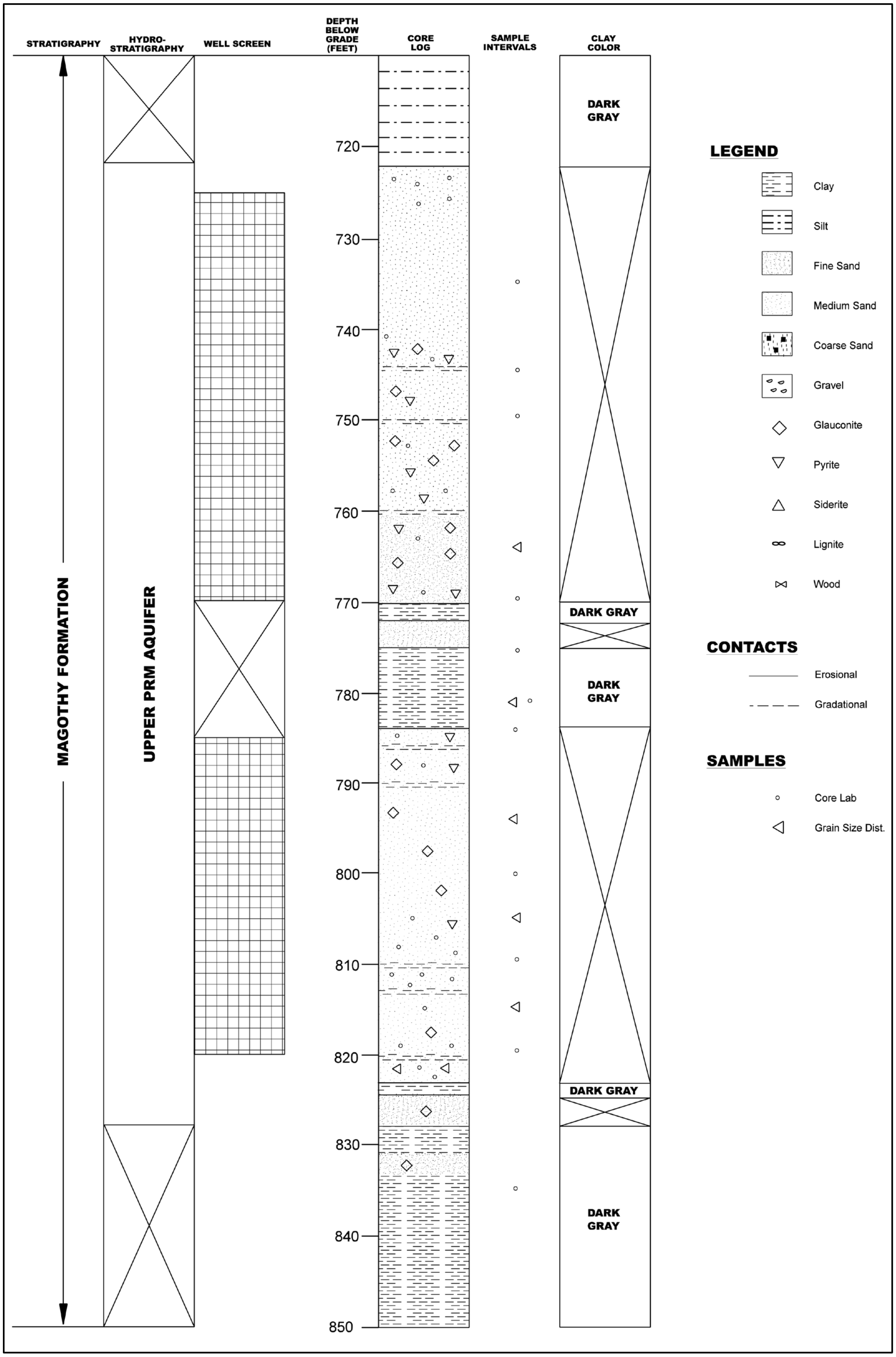


Figure 4-13. Example Graphic Log for Formation Samples Collected from Potomac Raritan Magothy Aquifer in New Jersey.

Typical criteria regarding sample selection for laboratory analysis comprises the following:

- One sample of confining bed above each aquifer, preferably within 5 foot of contact.
- One sample of confining bed below each aquifer, preferably within 5 foot of contact.
- Intervals distributed equally through permeable fraction of aquifer material.
- Intervals displaying mineral-rich zones within permeable fraction of aquifer material.

Field personnel can modify these criteria to match the recovery percentages achieved in aquifer materials, or intervals of interest within the aquifers.

4.4.1.1 Laboratory Analysis

The laboratory should analyze all core or cutting samples for bulk and clay fraction by XRD, inductively couple plasma mass spectrometry (ICP-MS), and XRF or energy dispersive x-ray (EDX) analysis to characterize the samples mineralogic and elemental composition, respectively. At locations where investigators have concerns with trace metals such as arsenic and selenium, the analyses require using ICP-MS, or methods sensitive to concentrations less than 1.0 mg/kg. XRF and EDX typically do not display such sensitive detection limits.

Although mineral and elemental composition remain important in every analysis, samples should undergo supporting analyses according to their composition and hydrologic significance (aquifer, confining bed, intra aquifer clay, etc.). Most labs specializing in analyzing core/cutting samples offer the following recommended analyses.

In aquifers composed of sand, samples should undergo the following analyses:

- Quantitative thin section petrography (300-point count, and pore-filling composition): Quantitative thin section petrography identifies mineralogy like XRD, but also characterizes texture, shape, porosity, cements, trace minerals, carbon content, etc. In unconsolidated samples, point counts accurately quantify porosity.
- Cation ion exchange capacity (CEC): CEC identifies cations in the exchange position of minerals and quantifies their tendency to exchange for other cations. CEC typically increases in proportion to the clay content of the sample.
- Scanning electron microscopy (SEM): SEM qualitatively looks at mineralogy, particularly the crystallinity of trace minerals and clays while supporting the description of pores and pore throat architecture.
- Laser particle size analysis: Laser particle size analysis provides an alternative to sieves for characterizing grain size distribution in sediments.
- Specific gravity: The specific gravity offers a simple test for determining the bulk density of samples, a common term in many analytical techniques.
- Acid digestible metals (ADM) or ICP-MS analysis
- Chromium reducible sulfur (CRS)
- Acid neutralization capacity

Because of the expense, consider requesting SEM analysis on a fraction (25 to 50 percent) of the total sand samples to obtain a representative portrayal of materials filling the aquifer interstices.

Aquifer materials consisting of limestone or dolomite should undergo the following (plus XRD, EDX, ADM, ICP-MS, CRS, and EDX):

- Qualitative thin section petrography
- SEM
- Core description: A core description suits describing the macro-properties of carbonate rocks including grain size, fossils, porosity, color, texture, etc.
- Helium porosity, air permeability, grain density, and lithology: Lithified samples support directly measuring porosity and permeability using compressed air
- Acid insoluble residue: Acid insoluble residue analysis determines the amount of material in a sample as a percentage that remains after dissolution with a strong acid
- Specific gravity

Focus SEM analysis on samples exhibiting primary porosity and/or discrete, mineral-rich intervals.

Samples originating from confining units should get analyzed for the following (plus XRD and EDX):

- Qualitative thin section petrography
- SEM
- Core description
- Cation exchange capacity
- Acid insoluble residue

Field personnel can modify these analytes to address intervals of interest within the aquifers and confining beds or modify for differing lithology like basaltic aquifers.

4.4.1.2 Bench, Batch, Leach, or Column Tests

Laboratory studies involving bench, batch, or column tests support evaluating reactions between recharge and the matrix of the receiving aquifer. Thus, these studies support developing an optimal recharge chemistry that either precludes reactions with aquifer minerals or promotes reactions that reduce a mineral's reactivity (passivate) in situ. The studies run the range between relatively simple batch tests run in an open beaker or glove boxes, or more sophisticated column tests simulating recharge as it migrates through an aquifer environment replicated in a cylindrical column.

Column tests can reproduce mixing between recharge and groundwater, acid-base reactions, redox reactions resulting in precipitation or dissolution of minerals, and pretreatment measures designed to passivate reactions. Yet, a column testing program can take months to complete with a corresponding increase in costs. Column tests require large volumes of aquifer material, custom-built columns, sophisticated monitoring equipment and more frequent laboratory analyses than simplistic batch testing. Moreover, mechanical difficulties like short circuiting of migrating recharge can negate results after months of testing. Thus, column tests appear more suitable to research or efforts that can accommodate extended testing periods.

Simpler batch and bench-scale tests can simulate a range of water-rock reactions. As an example, regarding arsenic mobilization, batch or leachability testing can reproduce sulfide oxidation, competitive desorption, cation exchange, and how an alkaline recharge pH can mobilize geogenic arsenic during MAR activities. Given differing recharge and groundwater chemistries inherent with MAR operations, multiple combinations of leaching studies could potentially support mitigating arsenic mobilization including:

- Control tests using no aquifer sediments
- Aquifer matrix with groundwater, or with recharge
- Adjusting pH to precipitate HFO or to enhance existing surfaces
- Adding oxidants to the recharge water
- Adjusting pH, plus oxidant addition
- Adjusting buffering capacity of recharge water
- Removing DO from recharge water
- Additives that mitigate cation exchange
- Testing competitive adsorption with phosphate and other oxy-anions
- Sterile vs. non-sterile

All lab tests can suffer regarding their realism in accurately reproducing field conditions. Even carefully prepared column tests usually involve loading cleaned and disinfected aquifer material into a cylindrical container. Yet, utilities should not over-complicate the answers sought from these tests. Most recharge contains dissolved oxygen, thus, over-emphasis on maintaining anoxic conditions when exposing aquifer minerals to recharge water can prove a wasted effort. In most cases the tests provide valuable data that supports further evaluation including modeling or developing pretreatment schemes to passivate reactive minerals in situ.

Control tests form a baseline for comparison with tests that entail changing the recharge chemistries. In alluvial sediments, passivating sulfide minerals and enhancing existing HFO coatings offers a proven method for adsorbing arsenic in migrating recharge mobilizing by sulfide oxidation, cation exchange and competitive desorption.

Passivating reactive sulfide minerals while precipitating adsorptive surfaces like HFO, involves elevating the pH above 8 in the presence of an oxidant. Often precipitating HFO produces an acidic pore water that can re-dissolve the HFO coating. Thus, employing a buffering agent can help arrest pH reduction while protecting adsorption surfaces. Adjusting pH, oxidant addition and buffer addition represent easy experiments for leaching studies.

Alternatively, in iron-poor environments, removing DO from the recharge water prevents oxidation of arsenic-bearing minerals. This method has proven effective at several sites in Florida. However, the method does not address competitive desorption or cation exchange reactions.

An expanding field of research in the geochemistry of aquifers undergoing MAR operations involves the activity of bacteria and other microbes. Thus, investigating biological activity will likely require maintaining sterile conditions during the collection, handling, storage and testing of aquifer samples.

Employing a modified version of ASTM International (ASTM) method D6234-13 (ASTM 2013) helps in completing leaching studies while providing legitimate, industry-accepted standards regarding procedures and interpretation. The method offers a rapid and economical approach to run multiple leaching tests that cover a broad range of recharge pretreatment techniques and even duplicative experiments to confirm findings.

4.4.2 Evaluation

The evaluation portion of the Phase 2 closely resembles equivalent processes from Phase 1 (Figure 4-1); however, field investigation results include actual aquifer minerals, amorphous phases, groundwater quality, and results from batch/bench testing. Knowing actual aquifer mineralogy allows more realistic geochemical modeling simulations, thus generating greater certainty in simulation results.

Except for issues related to recharge properties, by the end of the Phase 2, the field investigation should reveal the potential for nearly all geochemical reactions that may arise during MAR operations. Moreover, injection testing, if implemented, can realistically simulate well performance during MAR operations including the potential for various clogging issues like siltation, air binding, biofouling, and mineral precipitation. The flowchart representing Phase 2 contains several tabs that direct the user toward measures that can mitigate reactions involving arsenic or cationic metals during MAR operations (Figures 4-6 and 4-7). The flowchart describing cationic metals in the absence of arsenic provides a simplistic stepped approach for handling this common situation based on recharge chemistry.

By comparison, mitigating metal migration can prove more complex depending on recharge chemistry and conditions in the receiving aquifer. Thus, this section provides more explanation in navigating a pathway through the flowchart (Figure 4-6). The arsenic (or metal) mobilization flowchart contains two pages with the first page presenting combinations of recharge chemistry, aquifer geochemistry, reactions, and the potential results of the reactions. Page 2 offers pretreatment measures to mitigate arsenic mobilization reproducing the format from page 1.

Page 1 assumes arsenic takes two forms in an aquifer, contained as an accessory element in pyrite likely as arsenite (As (III)) or adsorbed to existing metal oxide surfaces in the aquifer as arsenate (As (V)). Because of the differing redox potentials required for each condition, As (III) and As (V) do not typically occur together (Dixit and Hering 2003). However, intervals or discrete micro-environments in an aquifer displaying differing redox potentials can host differing oxy-anions of arsenic (Figure 4-14).

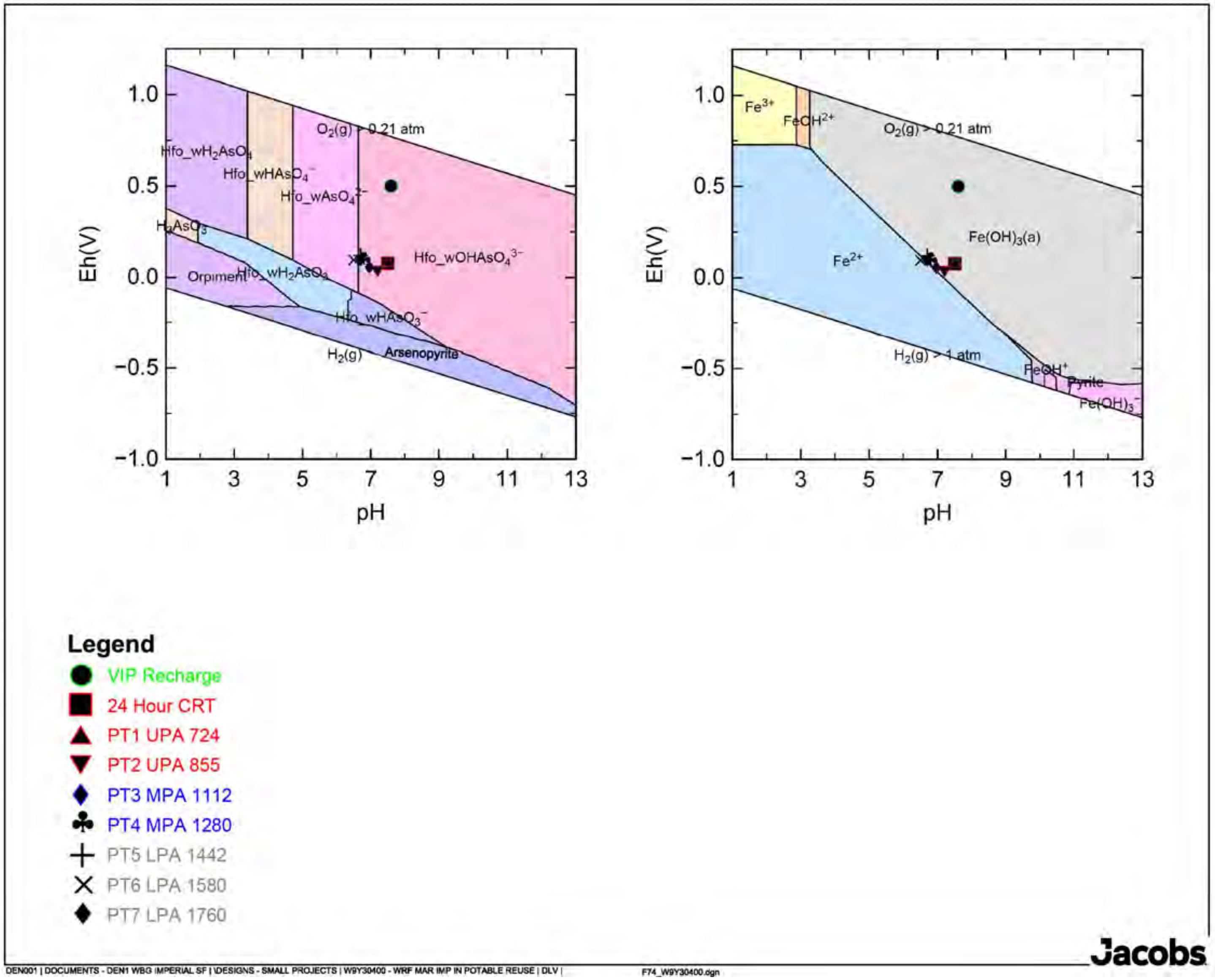


Figure 4-14. Arsenic and Iron Phase Diagrams Generated Using PHREEPLOT.

As (III) substitutes for sulfur in pyrite. The reaction for oxidizing arsenian pyrite with DO in recharge involves the following:

$$FeS_{2\text{-}}H_2AsO_3^{-1}+ 4O_2 + H_2O \text{ à } Fe^{2+} + (2)SO_4^{2-} + AsO_4^{3-} + 2H_2^{+}$$

The reaction liberates As (III) from pyrite, which eventually oxidizes to As (V) in most groundwater environments. Yet, the oxidation of As (III) to As (V) usually occurs very slowly (Evangelou 1995), particularly if recharge carries only DO, a relatively mild oxidant.

Studies on the composition of pyrite have shown a wide range of arsenic substitution (Jones and Pichler 2007; Kolker and Nordstrom 2009). In cores from Florida, XRF analysis indicated that arsenic substituted for sulfur in 10 percent of the available sites (Jones and Pichler 2007). However, other studies revealed significantly lower amounts of substitution, ranging between 0.1 and 1 percent by mass of total pyrite. The formula for pyrite with 1 percent by mass of arsenic equals:

$FeS_{1.984}As_{0.016}$, and for 0.1 percent by mass is $FeS_{1.9984}As_{0.0016}$.

If the recharge water displays a relatively reducing chemistry, pyrite will remain inert and not dissolve, leaving As (III) bound in pyrite. However, if the recharge water contains DO, pyrite oxidation may release ferrous iron, sulfate and As (III) (Figure 4-15). Pyrite oxidation represents a common mechanism for releasing arsenic or other metals (i.e., Co, Ni, Zn). In Florida, pyrite oxidation and other mechanisms have affected ASR operations for the last 20 years (Pyne 2005; Mirecki 2006). A common measure taken in aquifers containing pyrite, yet negligible amounts of other iron-bearing minerals (iron-poor environments) has involved removing DO from recharge. Physical removal employing a membrane de-gassing system has undergone testing in Florida but has suffered from operational problems and high costs (Kohn 2009). More recent testing involves stripping towers in removing DO.

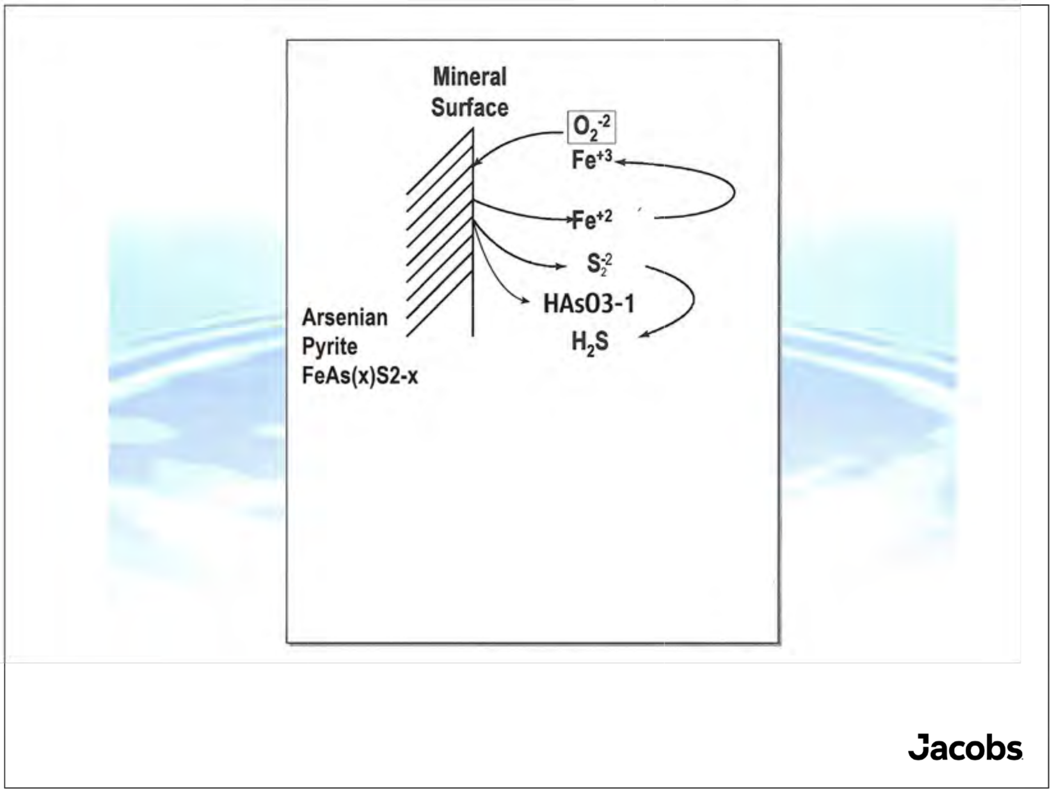


Figure 4-15. Conceptual Depiction of Pyrite Oxidation with As (III) Release.

Others (Pearce and Waldron 2010) have successfully limited arsenic production by adding hydrosulfide ($NaHSO_3$ and NaHS) products. However, the measure has resulted in significant iron production and the utility hosting the testing subsequently removed the system from service. Moreover, the reaction removing DO from recharge water using NaHS takes many hours. Thus, operators cannot measure DO removal after NaHS addition, but instead must rely on the reaction happening in the receiving aquifer.

Testing has successfully demonstrated the viability of removing DO to preclude pyrite oxidation in the iron-poor carbonate aquifers of Florida. Yet, in iron-rich environments more typical of sand and sandstone aquifers DO removal does not address competitive desorption of arsenic from existing metal oxide surfaces. Moreover, reduced recharge in absence of DO may promote arsenic dissolution through the reductive dissolution of metal oxides.

Accordingly, other measures work better in iron-rich aquifers such as adjusting the pH of recharge above 8, which rapidly precipitates HFO, coating the pyrite mineral surface, while reducing its reactivity (passivate). As oxy-anions, alkaline pH does not produce conditions favorable for adsorbing As (III) or As (V) released during pyrite oxidation, but increases the kinetics of passivating pyrite, locking arsenic in the mineral

Although not a subject of this report, combining elevated pH and DO works very well for passivating pyrite during ASR operations (Lucas 2012) in sand aquifers, preventing the recovery of arsenic along with iron and manganese. However, unidirectional flow during MAR operations creates differing conditions than ASR. During MAR, with fresh, unaltered minerals reacting with the recharge, pyrite oxidation can still control the chemistry at the leading edge of migrating recharge (Figure 4-16). Thus, elevated arsenic concentrations still may appear in monitoring wells located in the effective radius of a MAR well. However, the passivation of pyrite behind the leading edge of migrating recharge prevents the chronic leaching of arsenic. So, arsenic concentrations at a monitoring well typically peak for several days and then decline to background levels.

Recharge water containing oxi-anions like phosphate (PO_4^{-1}) can successfully compete with As (III) and As (V) on metal oxide surfaces (Neil, et al. 2012) in the receiving aquifer increasing arsenic concentrations in migrating recharge (Figure 4-17). Measures to mitigate competitive adsorption include removing PO_4^{-1} from the recharge water or maximizing the precipitation of metal oxide surfaces by employing the same technique used in passivating pyrite, like adjusting the pH above 8 in the presence of DO. Depending on PO_4^{-1} concentrations in the recharge water, maximizing HFO precipitation can prove a tenuous measure if PO_4^{-1} eventually occupies the majority of HFO sites. In applying this measure, arsenic can appear in a monitoring well as an attenuated agent many months after the leading edge of the recharge water plume has passed (Jacobs 2021).

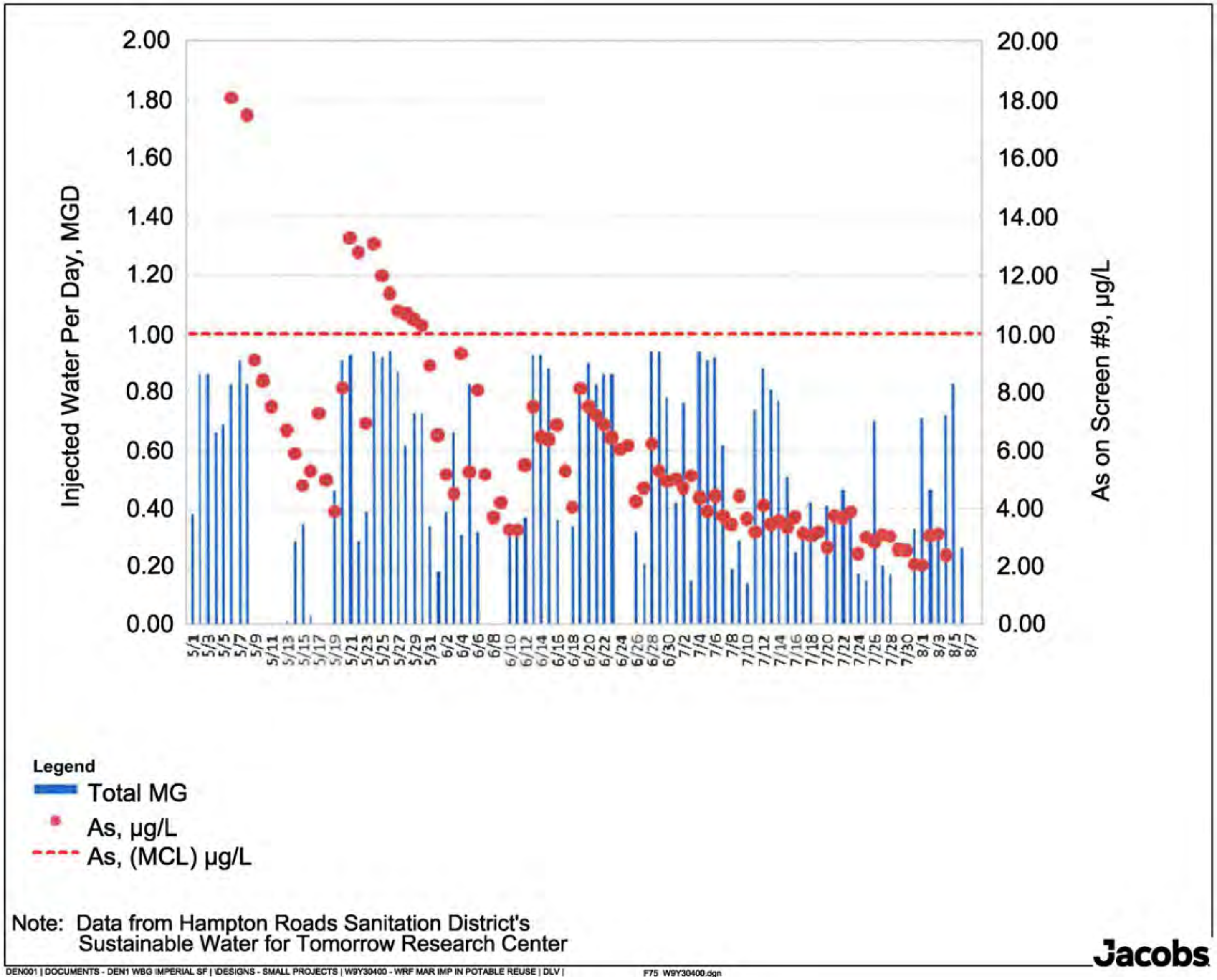
4.5 Phase 3—MAR Implementation and Operations

Implementing Phase 3 MAR operations entails activities prior to starting a new MAR facility and then long-term measures needed to maintain the facility (Figure 4-3) from a MAR well and geochemical monitoring perspective. To establish a baseline for groundwater quality, operators should collect three to six samples from each MAR well and monitoring well at intervals ranging from several weeks to one quarter prior to commencing MAR operations. Similarly, the utility should initiate a similar sampling program for the recharge water, yet, on a more compressed schedule. Sample analyses should consist of the list of analytes on PMCL and SMCL lists along with other parameters appearing on Table 4-1.

An important element for characterizing baseline conditions involves investigating the clogging potential of the recharge regarding TSS loading running MFI testing (Figures 4-18 and 4-10). MFI describes the slope of the line that shows the inverse of the flow rate (Figure 4-19 MFI curve) versus the amount of water that passes through a membrane filter containing 0.45 micrometer (µm) pores under constant pressure, standard temperature, and uniform filter area (Olsthoorn 1982).

Many researchers (Olsthoorn 1982; Hutchinson 1997; Buik and Willemsen 2002; Stuyfzand and Osma 2019; Schippers and Verrouw 1980) regard the MFI, referred to in this report as MFIs or MFI indices, as the best parameter to predict the clogging potential of an infiltrating water. Testing involves a relatively simple procedure of passing water through a 47-millimeter diameter membrane filter composed of 0.45 µm size pores until the flowrate declines to 20 percent of the rate measured at the beginning of the test. Individual tests last 30 to 45 minutes and thus, characterize particulate concentrations in recharge over a brief time interval.

Yet, MFI testing involves using a crude apparatus and time-consuming process often requiring two personnel to efficiently run the test. Moreover, air bubbles, pressure variations, and damage to the membrane filter too often compromise the results and make testing a challenging experience.



Note: Data from Hampton Roads Sanitation District's Sustainable Water for Tomorrow Research Center

Figure 4-16. Arsenic Concentrations at Leading Edge of Plume Passing Monitoring Well.

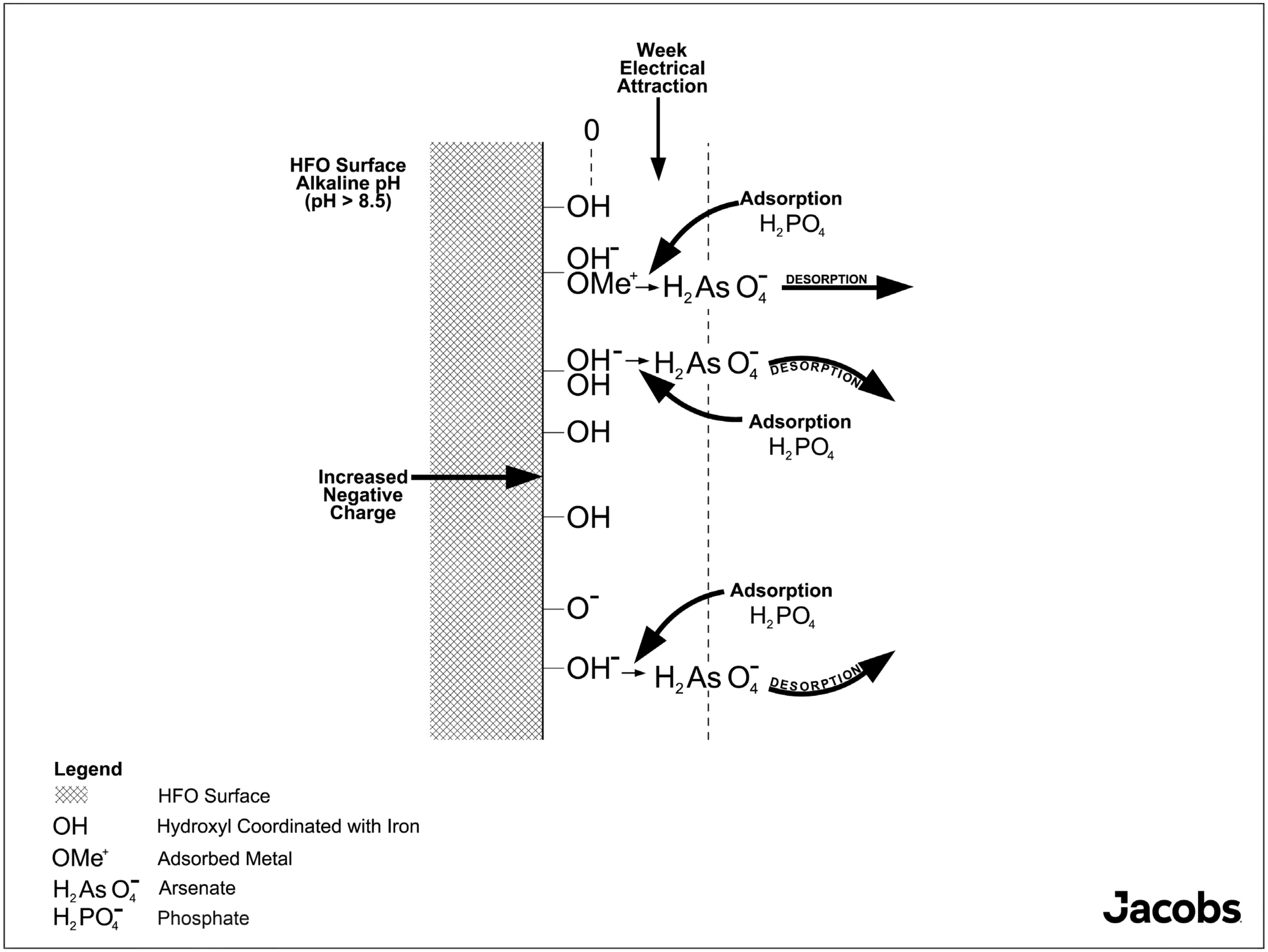
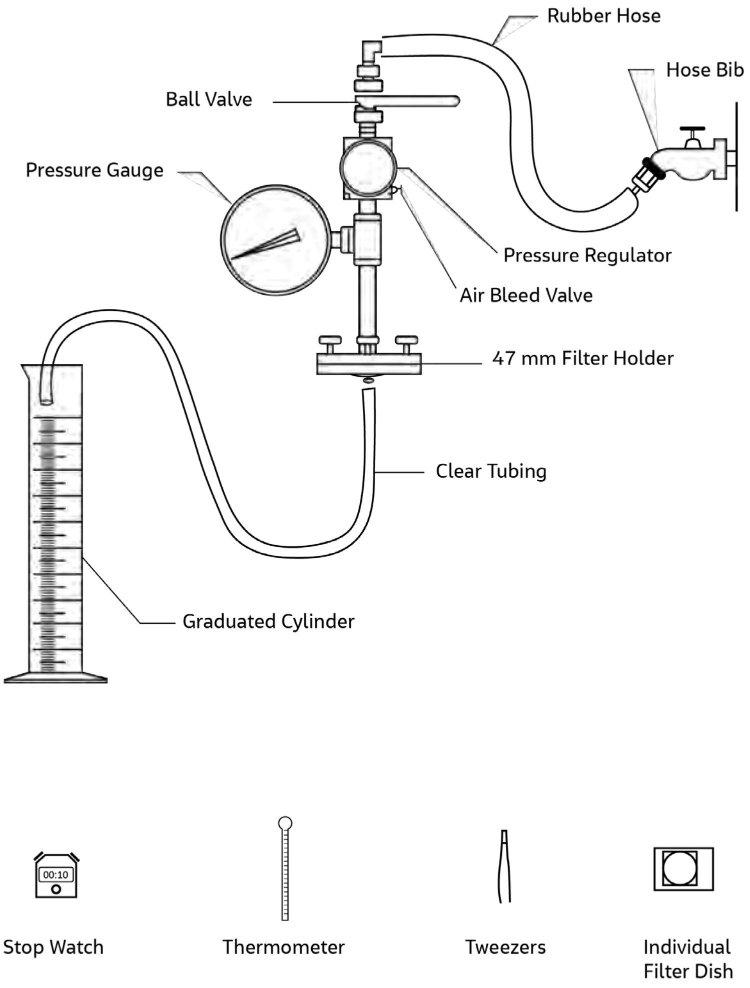


Figure 4-17. Conceptual Diagram of HFO Surfaces During Competitive Desorption Reactions.



Jacobs

Figure 4-18. Illustration of Membrane Testing Equipment.

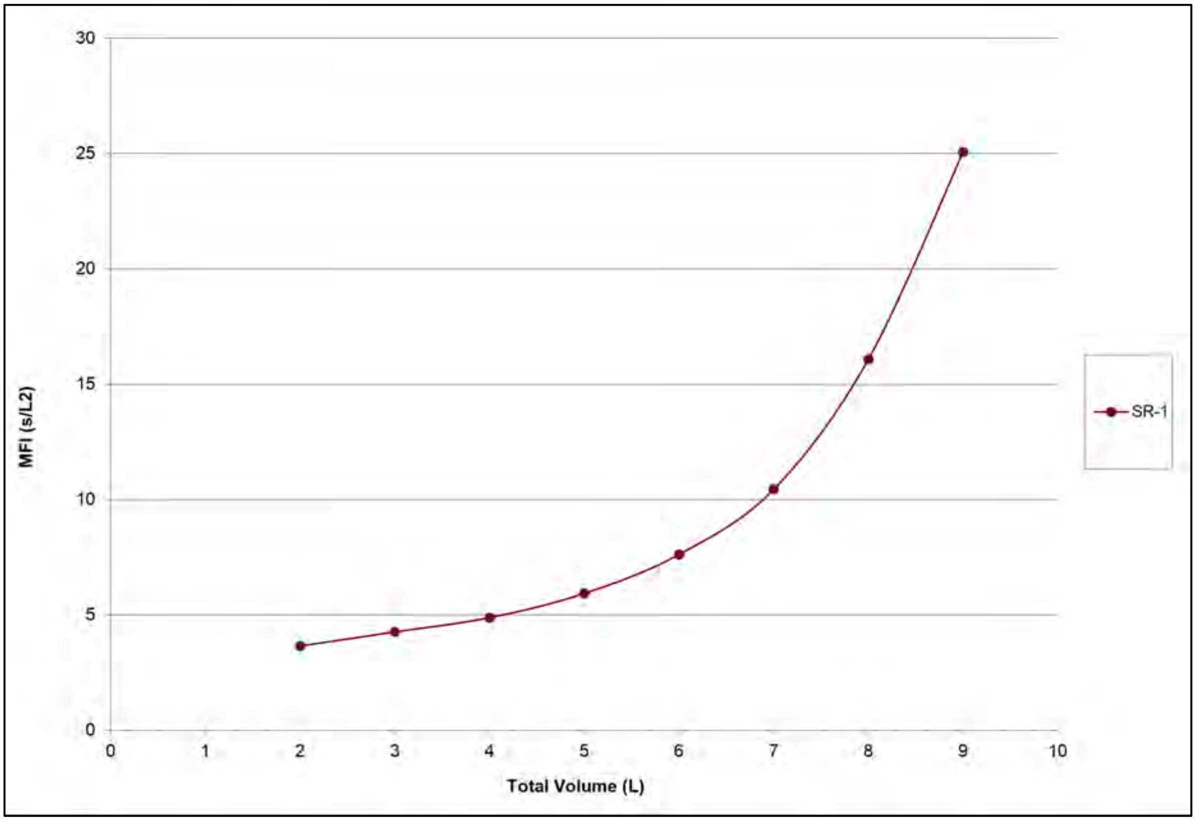


Figure 4-19. Example of MFI Data Curve.

Operators in Europe set an MFI of 3 sec/L^2 as an index (Hijnen, et al. 1998) for evaluating long-term MAR operations and the frequency of maintenance. A MAR facility producing recharge exhibiting an MFI below 3 sec/L^2 typically requires minimal maintenance to MAR wells like routine backflushing, non-invasive acidification or disinfection, or invasive rehabilitation (rehab) events. If the MAR facility returns MFI's routinely above 3 sec/L^2, the facility will likely require more maintenance including more frequent backflushing and invasive rehab every two to three years. Moreover, to mitigate the negative effects of accumulating particulates inherent to elevated MFIs, MAR operators should consider retrofitting MAR wellheads with filtration equipment like portable sand or bag filters.

A MAR facility should consider containing a station dedicated to MFI and bypass filter index (BFI) testing (Figure 4-20) with access to higher testing pressures through a booster pump and easy discharging of test effluent to a lab sink. Operators should run MFI and BFI tests at routine frequencies ranging from daily to weekly over the service life of the MAR facility.

BFI testing relies on the same underlying concepts as MFI tests in describing the inverse slope of the flowrate plotted against cumulative volume passing through a filter. Conversely, the BFI test employs a larger apparatus, and thus entails a longer test duration. Moreover, the filter elements display a pore size closer to 1 µm compared to the 0.45 µm used in MFI testing. BFI testing is performed through an apparatus situated across a pressure-reducing valve (PRV) on the wellhead or other piping. The inlet to the apparatus is situated upstream of the PRV with the outlet downstream. The BFI functions most effectively when the PRV sets the pressure to

30 pounds per square inch across the valve.

The BFI filter element consists of a 10-centimeter long, spun polyester cartridge filter mounted in a housing located upstream of a totalizing flowmeter. The flowmeter measures the flowrate and volume passing through the filter unit. To initiate a test, a new filter element is weighed (dry) to the nearest 0.001 gram and installed in the canister housing. After installing the filter, an operator will measure the flowrate through the flowmeter, at a daily frequency, until the rate declines to approximately 20 percent of the original rate. The length of a single test can run from several days for water containing higher TSS to several months for the cleanest recharge water. Operations personnel typically record flowrate through the BFI apparatus and water temperature once every 24-hour period.

Upon reaching the reduced flowrate, the filter is removed, dried, and weighed to the nearest 0.001 grams. A TSS concentration is calculated based on the difference in weights and flow volume through the filter apparatus. Another important use of the BFI element entails analyzing filtrate that accumulates on the filter to understand its composition and potential origin within the AWT.

4.5.1 Long-term Water Quality Monitoring

In the United States, the UIC program, whether regulated by the federal or state government, or specific state regulations often dictates locations and frequencies for sampling MAR facilities. The utility can implement their own test program to track constituents of interest migrating in the aquifer. UIC requirements typically involve sampling at monthly, quarterly, or annual frequencies for the recharge and recharge migrating through the aquifer in monitoring wells.

Analytes usually involve a limited list of interest to the regulating unit. Some utilities conduct their own sampling program at monitoring wells, using an extended list of analytes as shown in Table 4-1 until the leading edge of the recharge front passes a monitoring well, then reduces the list to conform with UIC or other local requirements.

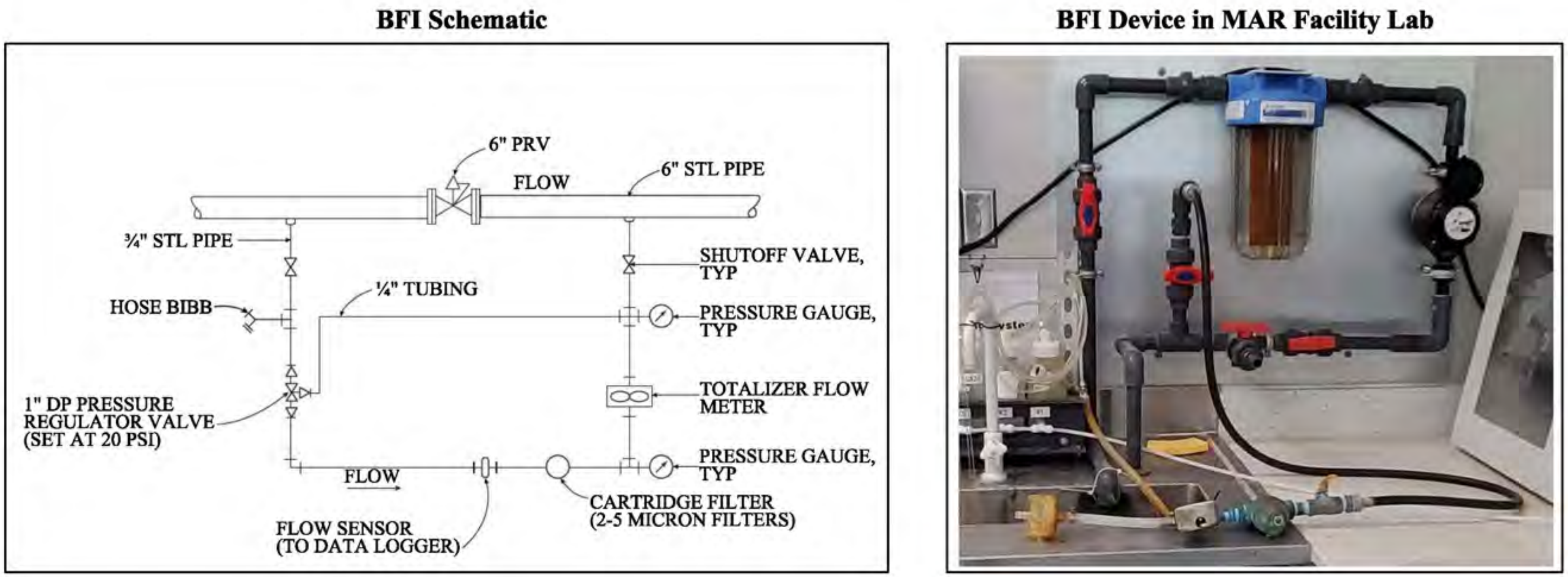
4.5.2 Geochemical Implications for Terminating MAR Operations

Conditioning an aquifer to passivate reactive metal-bearing minerals involves creating oxidizing conditions favorable to precipitating HFO. HFO, also called ferrihydrite or Fe(OH)3(a), describes an amorphous, loose, sticky material displaying great affinity for adsorbing metals and oxyanions according to the ambient pH (Cornell and Schwertmann 2003). HFO formed on minerals can dissolve if reducing conditions (redox, pH) return or increasing in crystallinity if oxidizing conditions persist in the case of prolonged MAR operations.

In a confined aquifer displaying ambient reducing conditions, halting MAR operations could conceptually result in restoring reducing conditions as native groundwater displaces the volume of recharge away from the former MAR facility. As reducing conditions return, HFO surfaces could dissolve releasing metals adsorbed during MAR operations. Although not covered in this project, ASR facilities that operate on seasonal cycles rarely leave large volumes of stored water in the aquifer. Thus, upon halting operations reduced conditions return to the storage zone within a few years (Lucas 2009), corresponding with increasing iron, manganese, and if present, arsenic concentrations.

However, at MAR facilities where utility does not recover water, the volume of migrating recharge can grow quite large along with dimensions of the body of migrating recharge. Body dimensions typically exceed 1 to 2 miles diameter after 10 years of operation. In the subsurface, HFO surfaces increase in crystallinity in sequence with lepidocrocite to goethite, to ultimately hematite, representing the most simplistic sequence. However, other researchers have documented many other mineral sequences (Cornell and Schwertmann 2003; Cornell and Schindler 1987; Brown et al. 1989). The more crystalline minerals exhibit less adsorption capacity but show greater resistance to dissolution under mildly reducing conditions (Stumm and Schulzberger 1992). Moreover, the more crystalline surfaces provide a more effective coating over the reactive mineral, permanently passivating the mineral underneath.

The redox potential in groundwater below MAR facilities operated by the utility partners to this project, exceeded iron-reducing conditions in only one instance while most displayed more oxidizing conditions with oxygen-reduction or nitrate-reduction typifying the prevailing redox processes (Table 3-13). Accordingly, restoring native redox potentials at these facilities would not likely result in releasing large amounts of metals from more crystallized iron oxide phases. Yet, groundwater in aquifers from Florida and elsewhere in the United States often display sulfate-reducing or methanic conditions. Thus, the return of native groundwater to the zone conditioned by MAR operations and could dissolve iron oxide minerals releasing undesirable or harmful metals in the groundwater. In summary, geochemical concerns over halting MAR operations can vary depending on the duration of MAR operations, the size of the migrating body of recharge, and ambient redox potentials in the native groundwater.



BFI Schematic

BFI Device in MAR Facility Lab

Figure 4-20. BFI Schematic and Testing Station in Lab at SRC.

CHAPTER 5

Conclusions

The project entailed characterizing the unique physical and geochemical issues encountered by utilities when planning, testing, or operating MAR systems. To constrain the scope of the project, the technical evaluation was limited to basins or wells receiving recharge purified to drinking water standards using AWT methods. Conceptually, the approach eliminated ASR or facilities that rely on storm or reclaimed wastewater as the source of recharge, yet some MAR facilities recharge a combination of AWT effluent, reclaimed water, stormwater or treated surface water.

Work performed for the project helped develop the following conclusions:

- Although utilities conduct MAR operations in a variety of aquifers including carbonate rocks and even crystalline rocks displaying primary porosity like extrusive igneous rocks, the project's utility partners, and most journal publications describe MAR operations in sand and sandstone aquifers.
- Clogging by particulates entrained in recharge, although not a strictly geochemical process, seemed to influence MAR operations in basins and wells at all the facilities evaluated for this project.
- Mitigating clogging in basins entails periodic drying and scraping with occasional sediment removal.
- With the well bore exemplifying a significantly smaller surface area than the infiltration area of a basin, MAR wells show greater sensitivity to clogging by solids. As operators cannot visually observe clogging in MAR wells, they must remain vigilant through other methods like tracking injection levels, injectivities and the results from MFI testing to determine maintenance frequencies.
- Recent research in ASR and MAR wells show that recharge displaying MFI indices exceeding 3 sec/L^2 prompts greater maintenance frequency for MAR wells including periodic backflushing and invasive well rehabilitation. Accordingly, the Decision Framework developed for this project relies on the MFI index to provide a quantitative threshold in recommending maintenance frequencies for MAR wells.
- Geochemical issues like clay dispersion can influence the operating characteristics of MAR facilities while metals mobilization in migrating recharge influences water quality in the aquifer and thus, the environmental viability of a MAR project.
- Recharging fresh water into an aquifer containing brackish or saline groundwater can cause clay dispersion and migration if the ionic strength of the groundwater exceeds the recharge by one order of magnitude.
- In fine or medium grained sand aquifers, ASR and MAR wells have suffered catastrophic, irreversible permeability losses (formation damage) when recharging water of significantly lower ionic strength than the native groundwater.

- In coarser-grained aquifers displaying larger pore spaces with excellent connectivity, clay dispersion may not present as great an issue. As an example, utilities in Southern California have recharged fresh water into brackish aquifers to prevent saltwater since the 1960s with no evidence of formation damage.
- The Decision Framework, narrative in the report and Case Studies provided in Appendix C all describe how a utility can take the proper measures to prevent formation damage.
- Of the utility partners, only one operating facility has implemented these measures or shown the recharge and groundwater conditions requiring measures to prevent clay dispersion. However, several facilities in planning should consider implementing these measures.
- Several facilities displayed issues with releasing cationic metals from reactive aquifer minerals during MAR operations. Typically, samples of migrating recharge at nearby monitoring wells displayed geochemical evidence of pyrite oxidation like declining pH and alkalinity and increasing sulfate along with the release of iron, manganese, cobalt, nickel, or zinc.
- The Decision Framework provides measures for treating reactive minerals in situ including pH adjustment, oxidant addition, and raising the buffering capacity of migrating recharge. These actions precipitate HFO surfaces that passivate reactive mineral surfaces, while building an adsorptive surface displaying a high affinity for fixing cationic metals.
- Conditioning aquifers to preclude clay dispersion or pretreating recharge to mitigate the release of cationic metals represent relatively straightforward solutions to the respective issues. By contrast, applying in situ measures to prevent the release of arsenic from minerals or surfaces can involve complicated combinations of measures depending on the ionic state of arsenic, redox conditions in groundwater and recharge, the presence of dissolved oxygen, and the presence of competitive anions like phosphate or carbonate in recharge. As an example, removing dissolved oxygen from recharge has proven effective at preventing pyrite oxidation and the release of arsenic. However, pyrite does not always represent the source of arsenic in an aquifer. Arsenic often adsorbs to metal oxide surfaces. So, removing DO from recharge may enhance reductive dissolution of metal oxide surfaces fixing arsenic in the aquifer, releasing arsenic into migrating recharge.
- The Decision Framework developed from the work of others and the authors of the report provides multiple pathways for handling arsenic in situ yet, remains unfinished work that will require augmenting over years of upcoming MAR operations.
- Although several utilities have operated MAR facilities for many years, the practice still appears relatively new and shows signs of growing rapidly worldwide. Thus, WRF should consider revising the work performed for the project periodically to reflect recent advances in technology and techniques for handling complex geochemical issues.

Appendix A

Literature Review

A.1 Aquifer Considerations and Mitigation Measures

This appendix contains the annotated bibliography for publications describing physical and geochemical issues experienced at MAR facilities, AWT water qualities, and water chemistry considerations. This appendix is organized alphabetically by topic and contains the citation and high-level abstract for each source.

A.1.1 Clay Dispersion, Clogging, and Stability

This section contains publications relevant to clay dispersion, clogging, and stability in groundwater wells, ASR wells, and other MAR applications. Other related topics include ionic strength, cation exchanged, clay formation, clay damage and plugging. The clay dispersion papers referenced are not focused on reclaimed water, however the papers are relevant because reclaimed water can have similarly low ionic strength (relative to saline aquifer) as the water used in these papers.

Brown, D. L., and W. D. Silvey. 1977. Artificial Recharge to a Freshwater-Sensitive Brackish Water Sand Aquifer, Norfolk, Virginia (Vol. 939). ***US Government Printing Office*****.**

> Researchers from the United States Geological Survey (USGS) conducted three Aquifer Storage and Recovery (ASR) test cycles (TC-1 through TC-3) at a site in Norfolk, Virginia during the early 1970s. USGS recharged potable water provided by the City of Norfolk, displaying an ionic strength of 0.02 moles/Liter (m/L) and a calcium bicarbonate chemistry, into a sand aquifer containing groundwater exhibiting an ionic strength of 0.5 m/L and a sodium chloride chemistry. The injection specific capacity (injectivity) of the test ASR well decreased by 80 percent within 90 minutes of initiating recharge operations. USGS determined that the differing ionic strengths and water chemistries between the recharge and groundwater caused interstitial clay minerals to disperse, migrate and eventually block port throats in the receiving aquifer. Despite the difficulties experienced during the project, USGS found that 85 percent of the injected water can be recovered if the well and aquifer clogging can be prevented.

Dillon, P., P. Pavelic, G. Massmann, K. Barry, and R. Correll. 2001). Enhancement of the membrane filtration index (MFI) method for determining the clogging potential of turbid urban stormwater and reclaimed water used for aquifer storage and recovery. ***Desalination*****, 140(2), 153-165.**

> This study applied the MFI, a standard test used to determine the rate at which water clogs a membrane filter, to turbid and organic-rich recharge waters to expand the use of this test to report clogging impacts for various water qualities. The study analyzed water qualities from 12 sites in Southern Australia for MFI, turgidity, total suspended solids (TSS), total organic carbon (TOC), particle size and scanning electron microscopy (SEM). The study helped characterize clogging potential of these specific types of water while improving the

precision of MFI for all water qualities.

Frenkel, H., J. O. Goertzen, and J. D. Rhoades. 1978. Effects of clay type and content, exchangeable sodium percentage, and electrolyte concentration on clay dispersion and soil hydraulic conductivity. *Soil Science Society of America Journal*, 42(1), 32-39.

This study determined the hydraulic conductivities along soil columns comprised of different soil types with varying salt concentrations. The results highlight that the main reason for reduced hydraulic conductivity is due to the clogging of soil column pores by dispersed clay particles.

Himes, R. E., E. F. Vinson, and D. E. Simon. 1989. Clay stabilization in low-permeability formations. In SPE Production Operations Symposium. *Society of Petroleum Engineers*. January.

This study investigated the effectiveness of a class of clay stabilizing treatment and additives, including conventional cationic organic polymers (COPs), on stabilizing formations with low permeabilities sandstone near the 10 millidarcy range. The results conclude that conventional COPs are not operative stabilizers for sandstone permeabilities less than 30 millidarcy and oligomers were more effective stabilizers for permeabilities less than 15 millidarcy.

Jeong, H. Y., S. C. Jun, J. Y. Cheon, and M. Park. 2018. A review on clogging mechanisms and managements in aquifer storage and recovery (ASR) applications. *Geosciences Journal*, 22(4), 667-679.

This review discusses challenges and solutions for clogging in artificial recharge systems, factors that accelerate clogging, preventive pretreatment measures, and rehabilitation methods. The paper highlights the necessary steps one should take prior to, during, and post installation and operation of an artificial recharge facility.

Katzer, T., and K. Brother. 1989. Artificial recharge in Las Vegas Valley, Clark County, Nevada. *Groundwater*, 27(1), 50-56.

This study investigated the feasibility of using managed aquifer recharge (MAR) to provide a more reliable water source to help the Las Vegas Valley Water District (LVVWD) meet their rising water demands. LVVWD conducted a MAR demonstration project using treated Colorado River water and observed the water chemistry and water-rock reactions, specifically focusing on calcite, to better understand the precipitating and clogging potentials of the injection wells in the groundwater system. The results highlight that there was no observed imbalance of calcium or other chemical constituents during the demonstration project.

McNab Jr., W. W., M. J. Singleton, J. E. Moran, and B. K. Esser. 2009. Ion exchange and trace element surface complexation reactions associated with applied recharge of low-TDS water in the San Joaquin Valley, California. *Applied Geochemistry*, 24(1), 129-137.

This study investigated various indicators such as stable isotope data, a dissolved gas tracer study, groundwater age dating, and geochemical modeling to better understand the effects of recharging high quality (low-Total Dissolved Solids [TDS]) water into a shallow aerobic

aquifer in California's San Joaquin Valley. Sufficient mixing occurred between the recharge water and the native ground water. The recharge water, with low-TDS, resulted in mobilization of oxyanionic trace elements and changed the proportion of ion exchange reactions in the receiving aquifer.

Mohan, K. K., and H. S. Fogler. 1997. Colloidally induced smectitic fines migration: existence of microquakes. *AIChE journal*, 43(3), 565-576.

This study investigated colloidally induced smectitic fine migration as a result of microquakes by developing a mathematical model used to predict the swelling behavior of smectites in aqueous solutions. The model compares permeability reduction, the transition of swelling from crystalline to osmotic regimes, as well as describes the impact of different cations on the transition. In addition to the mathematical model, x-ray diffraction was used to measure the changes in microstructure with varying salt concentrations.

Monaghan, P. H., R. A. Salathiel, B. E. Morgan, and A. D. Kaiser Jr. 1959. Laboratory studies of formation damage in sands containing clays. *Transactions of the AIME*, 216(01), 209-215.

This paper examined the how hydrocarbon-bearing formations change during the well construction process and how it impacts productivity. The results highlight that drilling has the potential to reduce productivity as a direct impact of low permeability surrounding the borehole. One example of where productivity needs to be restored is with clays, such as montmorillonite, because they swell on contact with fresh water.

Olsthoorn, T. N. 1982. The clogging of recharge wells, main subjects (p. 72). Keuringsinstituut voor Waterleiding Artikelen, *KIWA,* nv.

This paper presents guidelines for the design of well recharge systems including the prevention of clogging of recharge wells, permissible injection pressure, and redeveloping recharge wells.

Page, D., K. Miotliński, P. Dillon, R. Taylor, S. Wakelin, K. Levett, K. Barry, and P. Pavelic. (2011). Water quality requirements for sustaining aquifer storage and recovery operations in a low permeability fractured rock aquifer. *Journal of environmental management*, 92(10), 2410-2418.

This study investigated two topics: the impact of an ASR facility recharging stormwater into a low permeability fractured rock aquifer and the selection process of water treatment methods that can be used to prevent well clogging. The study looked at two different injection and recovery phases over a series of test cycles. The water quality from the potable water injection cycles was used to identify the pretreatment targets of turbidity and dissolved organic carbon for the harvested stormwater. To prevent well clogging, the study found that ultrafiltration and granular activated carbon performed best for removing suspended solids and nutrients as a pretreatment step to reduce physical and biological clogging.

Page, D., J. Vanderzalm, K. Miotliński, K. Barry, P. Dillon, K. Lawrie, and R. S. Brodie. 2014. Determining treatment requirements for turbid river water to avoid clogging of aquifer storage and recovery wells in siliceous alluvium. *Water research*, 66, 99-110.

The primary objective of this study was to identify the required pretreatment technologies such as bank filtration, coagulation, coagulation with activated carbon, and disinfection in addition to water quality targets that are needed for successful ASR practices. The research focused on injecting turbid source water into an aquifer comprised of medium to coarse sand. Soil column tested were conducted to assess the impact of various source water and the impact on the hydraulic conductivity. The results conclude that the active carbon vessels were the favorable pretreatment technology for prior to ASR injection for this specific case study.

Pavelic, P., P. J. Dillon, K. E. Barry, J. L. Vanderzalm, R. L. Correll, and S. M. Rinck-Pfeiffer. 2007. Water quality effects on clogging rates during reclaimed water ASR in a carbonate aquifer. *Journal of Hydrology*, 334(1-2), 1-16.

This study examined the rates of well clogging and water quality of the injectant at a reclaimed water ASR trial site located in a limestone aquifer in Southern Australia. The study spanned a four-year period where the water quality generally improved due to advancements in pretreatment. Key parameters like intrinsic permeability, turbidity, nutrients (total nitrogen, phosphorous, etc.), pH, particle filtration, microbial growth, and calcite dissolution were used to characterize the water quality following aquifer injection and were related to the rates of well clogging. The study concluded that injecting reclaimed water into a calcite rich aquifer resulted in microbial growth, particulate clogging during filtration, and unclogging by calcite dissolution.

Reed, M. G. 1972. Stabilization of formation clays with hydroxy-aluminum solutions. *Journal of Petroleum Technology*, 24(07), 860-864.

This study looked into treatment technologies to desensitize the exposure of sandstone cores with water. The results conclude that utilizing aluminum hydroxide solution can made the sandstone cores insensitive to fresh water when they are treated with hydroxy-aluminum solutions. The study recommends applying this solution as a field treatment to reduce clay dispersion and structural expansion.

Stuyfzand, P. J., and J. Osma. 2019. Clogging issues with aquifer storage and recovery of reclaimed water in the brackish Werribee aquifer, Melbourne, Australia. *Water*, 11(9), 1807.

The study from the City West Water in Melbourne, Australia addressed and monitored the risk of well clogging from injecting recycled water at two ASR pilot wells. The two main objectives involved optimizing methods to identify the TSS contribution from the recycled water injection and aquifer particles in backflushed water as well as utilized the MFI to predict the risk of biological and physical clogging.

Xia, L., Z. Gao, X. Zheng, and J. Wei. 2018. Impact of recharge water temperature on bioclogging during managed aquifer recharge: a laboratory study. *Hydrogeology Journal*, 26(7), 2173-2187.

The primary objective of this study was to investigate the impact of recharge water temperature through the experiment of two laboratory tests, one winter test and one summer test, to see the seasonal effects on the bio-clogging mechanisms and processes for

MAR. In the initial stages of the two experiments, the winter and summer tests showed rapid biologging due to the growth of bacteria cells and extracellular polymeric substances (EPS) production. The study found that in the winter test the total EPS reached its maximum concentration, primarily caused by an approximately 200 micrograms per gram sand increase, which was two times higher than the EPS production in the summer test. The study concluded that in the summer when temperatures are higher, the sand columns clogged approximately 10 times faster than in the winter due to the 10-fold bacterial growth rate.

A.1.2 Hydrogeochemical and Hydrological Considerations

This section contains publications relevant to hydrogeochemical and hydrological considerations and processes for groundwater recharge, MAR, recharge flux rates, artificial recharge, and ASR.

Abdelshafy, M., M. Saber, A. Abdelhaleem, S. M. Abdelrazek, and E. M. Seleem. 2019. Hydrogeochemical processes and evaluation of groundwater aquifer at Sohag City, Egypt. *Scientific African*, 6, e00196.

The aim of this study is to characterize hydrogeochemical characteristics and physicochemical properties of an Egyptian aquifer using the PHREEQC model to better understand the rock and water interactions. The model was coupled with a groundwater evaluation which revealed a deterioration of water quality was indicated by high concentrations of total dissolved solids, bicarbonate, calcium, and sodium, etc. The groundwater elevation and PHREEQC model supported one another, and various chemical concentrations correlations were used to identify the dissolution of halite minerals.

Antoniou, E. A., B. M. Van Breukelen, B. Putters, and P. J. Stuyfzand. 2012. Hydrogeochemical patterns, processes and mass transfers during aquifer storage and recovery (ASR) in an anoxic sandy aquifer. *Applied geochemistry*, 27(12), 2435-2452.

This study identified and quantified the hydrogeochemical processes that were observed at ASR test sites located in a confined anoxic sandy aquifer in the Netherlands. Oxic drinking water was recharged over 14 ASR cycles over a nine-year period. The study focused on the following reactions: oxidizing pyrite and sedimentary organic matter (SOM), adsorbing iron and manganese in multiple layers of the aquifer, dissipating carbonate minerals constrained in the lowest layer of the aquifer, as well as metals mobilization. The results highlighted that oxygen consumption by pyrite and SOM as well as ion exchange from the metals were the main factors that impacted the water quality.

Clark, J. F., S. H. Urióstegui, R. K. Bibby, B. K. Esser, and G. Tredoux. 2016. Quantifying apparent groundwater ages near managed aquifer recharge operations using radio-sulfur (^{35}S) as an intrinsic tracer. *Water*, 8(11), 474.

This study applied the cosmogenic radioisotope sulfur-35 (^{35}S) as a chronometer near two independent spreading basins that use recycled water for MAR sites in South Africa and California. The study found that the ^{35}S was detected in the source water and wells close to the spreading basins, highlighting that this was an effective tracer throughout the spreading pathway. As a result, the ^{35}S chronometer has the potential to be a valuable tool for managing MAR sites where regulatory incentives require minimum retention time. This study also recommends monthly to semimonthly sampling to capture the temporal variations and highlights the need for more robust groundwater age models.

De Vries, J. J., and I. Simmers. 2002. Groundwater recharge: an overview of processes and challenges. *Hydrogeology Journal*, 10(1), 5-17.

This paper provides an extensive review of the existing literature surrounding groundwater recharge. The key processes and challenges reviewed in this work include recharge-evaluation problems, recharge flux, water balance considerations, and hydraulic properties. The paper focused on semi-arid regions due to importance of groundwater in their water supply and how recharge varies in these climates.

Vanderzalm, J. L., D. W. Page, K. E. Barry, and P. J. Dillon. 2010. A comparison of the geochemical response to different managed aquifer recharge operations for injection of urban stormwater in a carbonate aquifer. *Applied Geochemistry*, 25(9), 1350-1360.

This study investigated the hydrogeochemical processes and effect on water quality that are impacted by recycling stormwater via aquifer storage transfer and recovery (ASTR) in a carbonate aquifer. The water quality parameters were observed during a two-part aquifer flushing scenarios. The first scenario looked at separate wells for injection and recovery thus meeting the definition of ASTR. The second scenario looked at a single well for both injection and recovery resembling ASR. The study compared the two MAR techniques (ASTR and ASR) impact on calcite dissolution, redox reactions and processes, and nutrient removal and recycling.

Ye, X., R. Cui, X. Du, S. Ma, J. Zhao, Y. Lu, and Y. Wan. 2019. Mechanism of suspended kaolinite particle clogging in porous media during managed aquifer recharge. *Groundwater*, 57(5), 764-771.

This study investigated the effect of water chemistry on physical clogging of wells during MAR by analyzing the hydrogeochemical mechanisms of saturated porous media. Three column experiments were conducted using kaolinite solids with the addition of calcium chloride/sodium chloride to assess the impact of clogging on surface filtration, inner blocking, attachment, hydraulic conductivity, and ion exchange. The results highlight the influence of ionic strength on recharge clogging and the mechanisms of solids clogging during MAR.

A.1.3 Lithological Profiling

This section contains publications relevant to lithological profiling, water-sediment reactions, water sensitivity, and swelling issues for groundwater practices.

Descourvières, C., N. Hartog, B. M. Patterson, C. Oldham, and H. Prommer. 2010. Geochemical controls on sediment reactivity and buffering processes in a heterogeneous aquifer. *Applied Geochemistry*, 25(2), 261-275.

This study characterized the heterogeneity and reductive capacity of injecting oxic water into an anoxic aquifer that is used for water reuse projects by investigating the water-sediment interactions based on the varying aquifer layers and quantifying the relationship between the reductive capacity and lithologies. The research looked at different reductive capacities for sands, clays, and silts using total organic carbon and pyrite concentrations present in the sediment. The results found that utilizing simplistic lithology failed to provide an explanation on the reductive capacities of the sediment. In contrast, the results highlight the importance of conducting a detailed geochemical analysis which highlights the key processes that contribute to the water quality of the aquifer.

Hewitt, C. H. 1963. Analytical techniques for recognizing water-sensitive reservoir rocks. *Journal of Petroleum Technology*, 15(08), 813-818.

The focus of this study was to better under the presence, cause, and magnitude of water sensitivity that impact water-rock reactions during recharge. Swelling of clays and plugging are two mechanisms that damage the recharge ability. The study recommends utilizing the following techniques to conduct a complete water sensitivity analysis: permeability measurements, physical swelling tests, x-ray identification of non-clay and clay minerals, and microscopic examination.

A.1.4 Metals Mobilization

This section contains publications relevant to metals mobilization, reactive transport models, pretreatment techniques, pyrite oxidation as well as other redox conditions and processes.

Antoniou, E. A., P. J. Stuyfzand, and B. M. van Breukelen. 2013. Reactive transport modeling of an aquifer storage and recovery (ASR) pilot to assess long-term water quality improvements and potential solutions. *Applied geochemistry*, 35, 173-186.

This study developed a reactive transport model to better comprehend the main hydrogeochemical processes that occur with trace metals when aerobic water is injected into an anoxic aquifer during ASR. The parameters and reactions of interest in the model include pyrite oxidation, calcite dissolution, surface complexation, iron and manganese precipitation as well as soil organic matter. A sensitivity analysis was conducted to determine which parameters controlled the rates of reactions and mobilization.

Antoniou, E. A., N. Hartog, B. M. van Breukelen, and P. J. Stuyfzand. 2014. Aquifer pre-oxidation using permanganate to mitigate water quality deterioration during aquifer storage and recovery. *Applied geochemistry*, 50, 25-36.

This study investigated the impact of aquifer pre-oxidation using permanganate with an oxygenated water in a column test to simulate groundwater recharge and see the impact on water quality and quantity of recovered water at an ASR site. The results highlight that pretreatment improved the net recovery ratio up to 84 percent when using oxygenated water and that pyrite oxidation decreased by 64 percent when using permanganate treatment.

Antoniou, E. A., B. M. van Breukelen, and P. J. Stuyfzand. 2015. Optimizing aquifer storage and recovery performance through reactive transport modeling. *Applied Geochemistry*, 61, 29-40.

This study utilized an existing reactive transport model (PHREEQC) to investigate water quality deterioration and efficacy of pretreatment during ASR operations. The model uses three different source waters including pre-treated drinking water, desalinated seawater, and urban stormwater to simulates the impact on iron, manganese, and arsenic when injected into an anoxic aquifer. The results highlighted that the water quality of the source water directly impacted which metals were released during ASR. The results highlight the importance of using a reactive transport model to better understand the mechanisms and reactions associated with ASR.

Blunden, B., and B. Indraratna. 2001. Pyrite oxidation model for assessing ground-water management strategies in acid sulfate soils. *Journal of Geotechnical and Geoenvironmental Engineering*, 127(2), 146-157.

This study developed a theoretical method to calculate the pyrite oxidation that occurs in acid sulfate soil by using a macropore/matric structure. The method takes into consideration the vertical oxygen transport and lateral oxygen diffusion through and into the soil macropores and matrix. The study coupled the theoretical method with a numerical approach that was developed using the computer simulation model ACID3D.

Darling, B. K. 2016. Geochemical factors controlling the mobilization of arsenic at an artificial recharge site, Clearwater, Florida. *Journal of Contemporary Water Research & Education*, 159(1), 105-116.

This study explored ion chemistry and oxidation-reduction reactions that contribute to arsenic leaching into the groundwater at an artificial groundwater recharge site that is in development in Florida. These results of this study are in agreement with the existing literature such that oxidation-reduction reactions control the stability of metals such as arsenic and iron and that it is imperative to assess the lithological, stratigraphic, hydrogeological, and geochemical characteristics of the aquifer of interest prior to recharging.

Fakhreddine, S., J. Dittmar, D. Phipps, J.Dadakis, and S. Fendorf. 2015. Geochemical triggers of arsenic mobilization during managed aquifer recharge. *Environmental science & technology*, 49(13), 7802-7809.

This study furthered the work of metals mobilization during MAR by examining the geochemical processes controlling arsenic desorption and mobilization In a shallow aquifer in Southern California. The study conducted several batch and column test experiments to analyze the recharge water chemistry with the goal to try and minimize the propensity of arsenic desorption. The results highlight that divalent cations, including calcium and magnesium, limit the arsenic desorption and enhance the adsorption potential for arsenic to adhere to phyllosilicate clay minerals in the aquifer.

Hallberg, R. O., and R. Martinell. 1976. Vyredox—in situ purification of ground water. *Groundwater*, 14(2), 88-93.

This study used the Vyredox method for in situ purification of metals that can be found in groundwater. The Vyredox method oxidizes ferrous iron to ferric by using iron-oxidizing bacteria and aeration wells allowing for the iron to transform from a soluble to insoluble form so that it can be removed prior to injecting the water into the groundwater well. The Vyredox method provides suitable in situ treatment for reactive minerals and metals which aid to higher water quality for recharge water during ASR and MAR operations.

Jin, J., A. R. Zimmerman, S. B. Norton, M. D. Annable, and W. G. Harris. 2016. Arsenic release from Floridan Aquifer rock during incubations simulating aquifer storage and recovery operations. *Science of The Total Environment*, 551, 238-245.

This study focused on the mechanisms that cause trace metals such as arsenic to release from a limestone aquifer during ASR operations in Florida. Over a 110-day period, laboratory incubated rocks and core material were analyzed under various conditions (aerobic, anoxic, anaerobic) to assess the level of arsenic release. The results found that the changing conditions provided different levels of reductive dissolution, oxidative dissolution, and desorptive arsenic release. The study concluded that arsenic release was not impacted by biotic processes.

Jones, G. W. 2015. Investigation of the Mechanisms for Mobilization of Arsenic in Two ASR Systems in Southwest Central Florida.

This dissertation focused on the naturally occurring arsenic from limestone that is leached into groundwater at an ASR site in Florida and what factors contribute to the release of the metal. The paper provided a review of the mechanisms that cause arsenic mobilization and recommendations for how to prevent the release of arsenic during ASR operations.

Mettler, E., M. Abdelmoula, E. Hoehn, R. Schoenenberger, P. Weidler, and U. Von Gunten. 2001. Characterization of iron and manganese precipitates from an in-situ ground water treatment plant. *Ground Water Monitoring and Remediation*, 39(6), 921-30.

This study characterized in situ treatment for iron and manganese precipitates in groundwater treatment. The results found that iron was oxidized into ferric oxide while manganese did not oxidize and instead deposited manganese oxides. The study further characterized the minerals based on their crystalline structure as well as the chemical and physical properties. This study provided insight on well clogging from these two minerals.

Mirecki, J. E., M. W. Bennett, and M. C. López - Baláez. 2013. Arsenic control during aquifer storage recovery cycle tests in the Floridan Aquifer. *Groundwater*, 51(4), 539-549.

This study conducted three test cycles to better understand the arsenic mobilization as a result of pyrite oxidation that could occur at an ASR location and to evaluate the ASR system performance at the Upper Floridian Aquifer and Kissimmee River ASR pilot system. The results indicate that arsenic sequestration occurs as a result of iron sulfide and iron oxide present in the recharge water during the recovery and storage phase of ASR.

Neil, C. W., Y. J. Yang, and Y. S. Jun. 2012. Arsenic mobilization and attenuation by mineral–water interactions: implications for managed aquifer recharge. *Journal of Environmental Monitoring*, 14(7), 1772-1788.

This paper reviews the arsenic sources and sinks entering, exiting, and within an aquifer that can lead to arsenic mobilization causing limitations for MAR. This paper provides detailed information on mineral–water interaction, physiochemical, biological, and hydrological processes that impact arsenic mobilization and attenuation. The paper presents recommendations on how to limit, predict, and monitor arsenic mobility for MAR operations.

Neil, C. W., Y. J. Yang, D. Schupp, and Y. S. Jun. 2014. Water chemistry impacts on arsenic mobilization from arsenopyrite dissolution and secondary mineral precipitation: implications for managed aquifer recharge. *Environmental science & technology*, 48(8), 4395-4405.

This study aimed to provide insight on the mechanisms that cause arsenic mobilization in groundwater as well as characterize conditions relevant to MAR operations. A bench-scale study experimentally determined activation energies under aerobic conditions for arsenic with wastewater secondary effluent. The outcomes of this bench-scale study can be useful for developing reactive transport metals for arsenic in MAR.

Neil, C. W. 2015. Understanding the Nano- and Macroscale Processes Impacting Arsenic Mobilization during managed aquifer recharge using Reclaimed Wastewater.

This dissertation paper investigates the mechanisms by which arsenic is released from natural sediment present in an aquifer during MAR on both a nano and macro scale. The research included in situ studies looked at the relationship between water parameters present in MAR such as natural organic matter and the impact on iron (III) (hydr)oxides nucleation and growth. On the micro scale, the research consisted of secondary mineral precipitation, phase transformation, and dissolution for wastewater systems while taking into account the impact of chloride.

Neil, C. W., M. J. Todd, and Y. J. Yang. 2018. Improving arsenopyrite oxidation rate laws: implications for arsenic mobilization during aquifer storage and recovery (ASR). *Environmental geochemistry and health*, 40(6), 2453-2464.

This study aims to better characterize and model arsenic remobilization at ASR and artificial recharge sites by compiling and analyzing available kinetic data on arsenic mobilization from arsenopyrite under different aqueous conditions.

Norton, S. B. 2011. Evaluating trace metal mobilization during managed aquifer recharge (Doctoral dissertation, University of Florida).

The dissertation sought out to prove that utilities can mitigate the mobilization of arsenic in aquifer storage by the removing primary oxidizers such as DO and chloramine from recharge water. The dissertation investigated the level of removal of primary oxidizers by researching different treatment technologies such as membrane filtration and degasification and air stripping towers to prevent arsenic mobilization. The paper highlighted that membrane degasification removed 99.93 percent of the DO and 90 percent of the chloramines.

Prommer, H., J. Sun, L. Helm, B. Rathi, A. J. Siade, and R. Morris. 2018. Deoxygenation prevents arsenic mobilization during deepwell injection into sulfide-bearing aquifers. *Environmental science & technology*, 52(23), 13801-13810.

The authors conducted a series of push-pull tests to pretreat the coproduced water from coal seam gas extraction prior to injecting it into a deep aquifer. The pretreatment included acid amendment or deoxygenation to identify and mitigate the risk of mobilizing metals and metalloids during the injection. The results found that regardless of a pH adjustment, the deoxygenated pretreatment method outperformed the acid amendment with respect to water quality and metals concentration of the injectant water.

Stolze, L., D. Zhang, H. Guo, and M. Rolle. 2019. Model-based interpretation of groundwater arsenic mobility during in situ reductive transformation of ferrihydrite. *Environmental science & technology*, 53(12), 6845-6854.

This study developed a modeling approach to better understand the different mechanisms that control the release of arsenic and ferrihydrite transformation in groundwater aquifers. The model considered different geochemical processes including both abiotic and biotic as well as surface complexation, sequestration, dissolution, and formation of secondary iron minerals. The modeling results highlight the importance of understanding how each geochemical process contributes to the overall arsenic mobilization within an aquifer and the interconnected relationships of the various parameters.

Sun, J., H. Prommer, A. J. Siade, S. N. Chillrud, B. J. Mailloux, and B. C. Bostick. 2018. Model-based analysis of arsenic immobilization via iron mineral transformation under advective flows. *Environmental science & technology*, 52(16), 9243-9253.

This study aimed to quantify the observed iron mineral (trans)formation and associated arsenic partitioning dynamics during the co-injection of nitrate and ferrous sulfate in arsenic-bearing sediments. The modeling results highlight that the primary driver for the fate and transport of arsenic is ferrihydrite formation as well as the reductive transformation that can occur before or after nitrate and ferrous sulfate injection. The study found that arsenic immobilization was dependent on the conversion from ferrihydrite to magnetite.

Vanderzalm, J. L., P. J. Dillon, K. E. Barry, K. Miotliński, J. K. Kirby, and C. L. G. La Salle. 2011. Arsenic mobility and impact on recovered water quality during aquifer storage and recovery using reclaimed water in a carbonate aquifer. *Applied Geochemistry*, 26(12), 1946-1955.

This study examined the fate, transport, and attenuation of arsenic during recharge into an ASR site by conducting first and fourth ASR test cycles of a full-scale field trial and looked at the water quality in the plume and receiving aquifer. The results found that the recovered arsenic concentration was greater than the source concentration indicating arsenic release from the natural sediments in the aquifer. The study also highlighted that the arsenic mobilization did not decline as the number of cycles increased.

Wallis, I., H. Prommer, C. T. Simmons, V. Post, and P. J. Stuyfzand. 2010. Evaluation of conceptual and numerical models for arsenic mobilization and attenuation during managed aquifer recharge. *Environmental science & technology*, 44(13), 5035-5041.

This paper used geochemical data from an injection experiment in the Netherlands to develop a conceptual and numerical model that evaluates trace metal mobilization during MAR. The data was for the injection of oxygenated water into an anoxic aquifer where arsenic mobilization was observed. After calibrating the reactive transport model, the results highlighted that arsenic release was observed during co-dissolution of arsenopyrite and was kinetically controlled by the oxidation of arsenic (III) and arsenic (V). Arsenic adsorption occurred during surface complexation of the neo-precipitated iron oxides.

Wu, X., B. Bowers, D. Kim, B. Lee, and Y. S. Jun. 2019. Dissolved organic matter affects arsenic mobility and iron (III)(hydr) oxide formation: implications for managed aquifer recharge. *Environmental science & technology*, 53(24), 14357-14367.

This study utilized bench-scale tests to observe how dissolved organic matter (DOM) mobilizes arsenic from arsenopyrite during a simulated MAR application. The results found that in the short-term, DOM decreased arsenic mobility due to dissolution, but in the longer time periods, increased arsenic mobility due to a reduced adsorptive capacity and inhibition.

A.1.5 Organics

This section contains publications relevant to organics, sedimentary organic matter, microbiology and biological fouling, biofilms, and trace organics.

Craig, L., J. M. Bahr, and E. E. Roden. 2010. Localized zones of denitrification in a floodplain aquifer in southern Wisconsin, USA. *Hydrogeology journal*, 18(8), 1867-1879.

This study looked into whether or not denitrification was occurring below the surface organic layer of a floodplain aquifer located within an agricultural watershed in Wisconsin. Major cations and other parameters such as nitrate, sulfate, chlorine, oxygen, and dissolved organic carbon were observed over a 1-year monitoring period and seventeen different groundwater samples were collected and analyzed for nitrate isotope compositions. The results highlight that denitrification was occurring in the subsurface layer, which contain available electron donors, as a result of the groundwater mixing zones that transport nitrate.

Linlin, W., Z. Xuan, and Z. Meng. 2011. Transformation of dissolved organic matter in a novel groundwater recharge system with reclaimed water. *Water environment research*, 83(12), 2140-2147.

This study investigated the removal and transformation of DOM in the system through laboratory-scale experiments using reclaimed water for groundwater recharge. The results highlight that biodegradation in the aerobic short-term vadose zone can reduced DOM and trihalomethane formation potential.

Niinikoski, P., S. Saraperä, N. Hendriksson, and J. A. Karhu. 2016. Geochemical and flow modelling as tools in monitoring managed aquifer recharge. *Applied Geochemistry*, 74, 33-43.

This research looked at the microbial decomposition of organic matter by studying the isotopic composition of dissolved inorganic carbon with calcite dissolution in recharge water in Finland. The goal of this study was to develop a method that can quantify the oxidative decomposition of organic matter and identify when the decomposition started in the aquifer. The results highlight that the organic matter concentration reduced by 30 to 50 percent in the infiltrated water.

Rauch-Williams, T., C. Hoppe-Jones, and J. E. Drewes. 2010. The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge. *Water research*, 44(2), 449-460.

This study investigated the relationship between bulk organic carbon matrixes and the impact on fate and transport of trace organic chemicals during MAR. Column experiments were conducted under aerobic and anoxic recharge conditions to better understand the infiltration rate, biological degradation, and contaminant removal. The results showed that the removal rates varied widely among the trace organic chemicals but found general trends that removal increased under aerobic conditions.

Vanderzalm, J. L., C. L. G. La Salle, and P. J. Dillon. 2006. Fate of organic matter during aquifer storage and recovery (ASR) of reclaimed water in a carbonate aquifer. *Applied Geochemistry*, 21(7), 1204-1215.

This research conducted a full-scale field trial using recycled water in two ASR cycles to better understand the fate of injected organic matter and subsurface redox reactions in a carbonated aquifer. The study observed that the redox state remained consistent with the injected water and native groundwater and thus that microbial activity plays a major role in predicting the redox reactions. The results highlight a 20 to 40 percent reduction of dissolved organic carbon in the injected water was observed dur to mineralization with DO and nitrate.

Wiese, B., G. Massmann, M. Jekel, T. Heberer, U. Dünnbier, D. Orlikowski, and G. Grützmacher. 2011. Removal kinetics of organic compounds and sum parameters under field conditions for managed aquifer recharge. *Water Research*, 45(16), 4939-4950.

This study aimed to provide a method to better quantify and interpret in situ removal efficiencies of organic compounds and other parameters at MAR sites. The study found that the improved removal efficiencies were correlated to the redox conditions, kinetics, and residual thresholds values and field/site characteristics.

Yoon, M. K., and Amy, G. L. 2015. Reclaimed water quality during simulated ozone-managed aquifer recharge hybrid. *Environmental Earth Sciences*, 73(12), 7795-7802.

This study tracked the level of removal of effluent organic matter and trace organic contaminants with the hybrid treatment technologies of ozonation combined with MAR using reclaimed wastewater or purified water from water reuse applications. The research conducted soil column experiments and batch reactors and performed chemical and bacterial analyses to assess the reclaimed water quality in this MAR application. The results suggest that adding ozonation to the MAR processes successfully and effectively removes effluent organic matter and trace organic contaminants compared to traditional MAR.

A.2 Managed Aquifer Recharge for Potable Reuse

A.2.1 Aquifer Injection

This section contains publications relevant to aquifer injection, groundwater recharge, seawater intrusion barrier, and the respective water quality implications.

Bral, K., W. Jackson, Y. Sim, and T. Mortonet. 2005. Innovative Approach for Automating Injection Well Systems, Case Study: Dominguez Gap Seawater Intrusion Barrier in Long Beach, California. 12th Biennial Symposium on the Groundwater Recharge, Tucson, AZ.

> This paper describes the Dominguez Gap Barrier Extension Project strategy and approach automating the seventeen MAR wells. Traditionally well rehabilitation and redevelopment procedures are executed on a manual basis. The automatic redevelopment process uses a technique called juttering, which is less intensive but must be completed more frequently. The system performance results highlight that the system can operate successfully in a fully automatic mode that incorporates local and removes controls.

CH2M HILL Engineers, Inc. (CH2M). 2016. Final Report Sustainable Water Recycling Initiative: Groundwater Injection Hydraulic Feasibility Evaluation (Report No. 1). Hampton Roads Sanitation District.

> This paper summarizes the hydraulic feasibility study conducted in Virginia on aquifer replenishment with using purified water from advanced treatment of wastewater secondary effluent for groundwater recharge. Mathematical models were used to understand the relationship between of wastewater treatment plant flow rate, injection well capacity, and transmissivity of the underlying aquifer. This study provided insight on strategies for determining the number of wells needs for MAR, the well capacity, well diameters, and inter-well spacing for five potential MAR facilities.

Schmidt, C. M., A. T. Fisher, A. Racz, C. G. Wheat, M. Los Huertos, and B. Lockwood. 2012. Rapid nutrient load reduction during infiltration of managed aquifer recharge in an agricultural groundwater basin: Pajaro Valley, California. *Hydrological Processes*, 26(15), 2235-2247.

> This study assessed the patterns of infiltration and nitrate loading rate during MAR in California. The results found that the nitrate concentration in the infiltrating water decreased because of the passage through the subsurface soils within the first meter of the aquifer. The study calls out the importance of denitrification on nutrient reduction loading as well as the variability observed due to spatial and temporal differences in the receiving water body.

A.2.2 Groundwater Management

This section contains publications relevant to groundwater management, MAR, groundwater mixing, water quality considerations, land subsidence, and water reuse applications.

Bekele, E., D. Page, J. Vanderzalm, A. Kaksonen, and D. Gonzalez. 2018. Water recycling via aquifers for sustainable urban water quality management: Current status, challenges and opportunities. *Water*, 10(4), 457.

> This paper provides a summary of the current status, challenges, and opportunities that are associated with MAR using advanced treated water. The focus of the paper is on large-scale MAR operations in Australia and other places around the world where MAR provides a feasible solution to seawater intrusion. The paper highlights the scientific areas where development has occurred including water quality assessment, aquifer characterization,

and microbiological activity within the aquifer.

P. Dillon, P. Stuyfzand, T. Grischek, M. Lluria, R. D. G. Pyne, R. C. Jain, J. Bear, J. Schwarz, W. Wang, E. Fernandez, C. Stefan, M. Pettenati, J. van der Gun, C. Sprenger, G. Massmann, B. R. Scanlon, J. Xanke, P. Jokela, Y. Zheng, R. Rossetto, M. Shamrukh, P. Pavelic, E. Murray, A. Ross, J. P. Bonilla Valverde, A. Palma Nava, N. Ansems, K. Posavec, K. Ha, R. Martin and M. Sapiano. 2019. Sixty years of global progress in managed aquifer recharge. *Hydrogeology journal*, 27(1), 1-30.

This paper aims to quantify and summarize the MAR applications and practices on a global scale as well as provide guidance and insight on the primary MAR techniques and advancements. The paper highlights the importance that MAR plays with combating groundwater depletion due to climate change, population growth, and other externalities.

Hellauer, K., D. Mergel, A. S. Ruhl, J. Filter, U. Hübner, M. Jekel, and J. E. Drewes. 2017. Advancing sequential managed aquifer recharge technology (SMART) using different intermediate oxidation processes. *Water,* 9(3), 221.

This study aimed to better understand the biotransformation of trace organic chemicals found in recharge water by employing advancing sequential MAR technology (SMART) during MAR. The researchers created four parallel laboratory-scale soil column experiments using different intermittent aeration techniques including ozone, pure oxygen, aeration with air, and no aeration to improve the transformation of the organic chemicals. The results depict that the organic chemicals were better removed during sequential filtration opposed to single step filtration, implying that SMART is an effective technique to use during MAR. Ozonation showed effective removal of the persistent organic chemicals.

Page, D., E. Bekele, J. Vanderzalm, and J. Sidhu. 2018. MAR in sustainable urban water management. *Water*, 10(3), 239.

This study draws attention to the importance of diversifying water sources in urban areas and highlights MAR as a sustainable solution to urban water management. The results emphasize the need to be resourceful and use the underutilized stormwater and advanced treated wastewater secondary effluent as recharge water. The paper highlights water quality challenges, intrinsic aquifer properties, and cost.

Smith, R., R. Knight, and S. Fendorf. 2018. Overpumping leads to California groundwater arsenic threat. *Nature communications*, 9(1), 1-6.

This study investigated the impact that groundwater pumping had on the observed release of arsenic, found in the natural aquifer sediments, in an aquifer in San Joaquin Valley of California. The paper concludes that there is no link between historic groundwater pumping and current groundwater aquifer concentrations, yet the results of the study suggest that arsenic resides in the pore water of clay strata which is released during pumping of an aquifer. One of the key takeaway messages is to be cognizant of groundwater pumping and that overpumping can lead to adverse water quality.

Spellman, Frank R. 2017. Land Subsidence Mitigation: Aquifer Recharge Using Treated Wastewater Injection. *CRC Press*.

This book examines the process of injecting treated wastewater into groundwater wells for the following beneficial reasons: slow or delay the process of land subsidence, aquifer replenishment, and mitigation of coastal flooding. The overarching goal of the book is to provide solutions to land subsidence due to excessive groundwater withdrawal. The concepts cover a wide range of topics and case studies including nutrient reduction in discharged waterways, how to provide a sustainable groundwater supply, techniques to reduce the rate of land subsidence, and tips for defending saltwater intrusion.

Stuyfzand, P. J., and A. Doomen. 2004. The Dutch experience with MARS (Managed Aquifer Recharge and Storage): a review of facilities, techniques, and tools. KIWA NV, Rijswijk, the Netherlands.

This report provides an inventory of various MAR and managed aquifer recharge subsurface storage (MARS) applications and operations across the Netherlands. The report includes tools, techniques, and mitigation strategies developed by Kiwa Water Research that can be used to diagnose, troubleshoot, and predict future consequences of MAR and MARS.

Stuyfzand, P. J. 2016. History of managed aquifer recharge in the Netherlands. Electronic Supplementary Material-Hydrogeology Journal Sixty years of global progress in managed aquifer recharge, 36.

This paper provides a detailed synopsis of the history of unmanaged and MAR in the Netherlands. The paper highlights different recharge techniques such as artificial recharge through basins, aquifer transfer recovery, aquifer storage and recovery, riverbank filtration, and MAR.

Thomas, B. F. 2018. Sustainability indices to evaluate groundwater adaptive management: a case study in California (USA) for the Sustainable Groundwater Management Act. *Hydrogeology Journal*, 27(1), 239-248.

This study created a groundwater sustainability framework that includes performance indicators and groundwater-level elevation records to be used to measure management strategy outcomes as a follow up requirement from the Sustainable Groundwater Management Act in California. The framework includes key metrics such as groundwater storage, spatial and temporal variability, climate change, groundwater use, etc. The intent is for this framework to be used to inform decision-making and identify future management strategies for groundwater management.

Yuan, J., M. I. Van Dyke, and P. M. Huck. 2016. Water reuse through MAR: assessment of regulations/guidelines and case studies. *Water Quality Research Journal of Canada,* 51(4), 357-376.

This paper highlights the viability and importance of using reclaimed water from a water reuse application for MAR. This paper provides an introduction on utilizing reclaimed water for MAR as well as a comparison of current regulations from a national and international perspective on water reuse. The framework includes design criteria, operation evaluation strategies, process overviews, risk assessments and other key metrics for successfully implementing MAR.

Yuan, J., M. I. Van Dyke, and P. M. Huck. 2019. Selection and evaluation of water pretreatment technologies for MAR with reclaimed water. *Chemosphere*, 236, 124886.

> This paper developed a multi-criteria approach to review, evaluate, and select a viable pretreatment technology for the removal of critical contaminants in reclaimed wastewater effluent for MAR systems. Treatment efficiency targets and credits were developed based on existing literature. Treatment scores were assigned based on treatability, cost, and sustainability. The outcomes provide groundwater agencies with an efficient selection process of pretreatment technologies for indirect potable reuse for MAR applications.

A.2.3 Aquifer Storage and Recovery

This section contains publications relevant to ASR, groundwater recharge, operational considerations, feasibility studies, performance factors, site selection, sensitivity analysis, and groundwater/aquifer management.

Bral, Kevin M., and Donald R. Kendall. 2006. The Development and Implementation of Aquifer Storage and Recovery in the North Los Posas Basin, Moorpark, California. CH2M HILL Engineers, Inc.

> This report provides information on the development history of the Calleguas ASR system which started operation in 1991. The vision for this project was to ensure water supply redundancy by utilizing underground storage in the aquifers. The ASR system currently contains two major wellfields and 18 ASR wells.

Bral, Kevin, T. Tangsutthinon, and S. Chusanathas. 2015. Demonstration Program to Mitigate Drought and Flooding in the Northern Part of the Chao Phraya River Basin, Thailand Using ASR Methods—Part 2. GEOINDO, 23 Nov. 2015.

> This paper summarizes an ASR test facility containing two recharge wells located in Thailand. The test program is split into two parts. Part 1 includes siting, construction, and commissioning of the facility. Part 2 includes the design criteria, test program details and hydrogeochemical testing methods as well as the challenges, results, and conclusions from this ASR application.

Brown, C. J., Ward, J., and Mirecki, J. 2016. A revised brackish water aquifer storage and recovery (ASR) site selection index for water resources management. *Water resources management*, 30(7), 2465-2481.

> This study applied dimensionless parameters to analyze the performance and physical behavior of a brackish water ASR site. A comprehensive literature review was performed to select three of the six dimensionless indices that can be used to predict water quality and performance of ASR. To validate the selection, the three parameters were applied to 29 different ASR systems in Florida and proved to be effective.

CH2M HILL Engineers, Inc. 2010. Phased implementation of a large-scale aquifer storage and recovery system in San Antonio, Texas, USA. Prepared for Texas Water Development Board, Austin, Texas.

> This presentation provides a step-by-step overview of the successfully implementation of a

large-scale ASR system in Texas. This ASR system was able to reduce the aquifer withdrawals during the summer months by 25 percent and mitigated evaporative losses and other adverse environmental impacts associated with surface water impoundment.

Chinnasamy, C. V., W. C. McIntyre, and D. C. Mays. 2018. Technical and administrative feasibility of alluvial aquifer storage and recovery on the South Platte River of northeastern Colorado. *Water Policy*, 20(4), 841-854.

This study looked into the feasibility of an alluvial ASR facility in the semi-arid state of Colorado by using a technical-administrative analysis that takes into consideration the water rights governed by the prior appropriation documentation. The technical feasibility consisted of a groundwater model, that accounting for well clogging, that was tested on a hypothetical recharge site. The administrative feasibility, the first of its kind among the literature, consisted of a legal availability of water from both recycled wastewater effluent and free water. This study emphasized the need to couple hydrologic analysis with policy and regulatory requirements.

Forghani, A., and R. C. Peralta. 2018. Intelligent performance evaluation of aquifer storage and recovery systems in freshwater aquifers. *Journal of Hydrology*, 563, 599-608.

This paper used artificial neutral network software to predict the recovery effectiveness of ASR wells in non-brackish aquifers. The model takes into consideration performance criteria for the injected water and receiving aquifer. The results highlight the importance of using computationally complex simulations to better understand the drivers, performance, and sensitivity of ASR applications in freshwater aquifers.

Otero, C. L., and B. L. Petri. 2010. Quality of Groundwater at and Near an Aquifer Storage and Recovery Site, Bexar, Atascosa, and Wilson Counties, Texas, June 2004-August 2008. US Department of the Interior, US Geological Survey.

This project conducted a four-year study to evaluate the water quality prior to and post-injection from the Carrizo aquifer and at an ASR site in Texas. Groundwater samples were obtained and analyzed for physical properties, geochemical and isotope data, water chemistry, metal mobilization and other water quality parameters. The study found that there was no significant shift in the water quality that was injected into the aquifer and transferred through a 38-mile pipeline to the ASR location.

Page, D. W., L. Peeters, J. Vanderzalm, K. Barry, and D. Gonzalez. 2017. Effect of aquifer storage and recovery (ASR) on recovered stormwater quality variability. *Water research*, 117, 1-8.

This study assessed the stormwater quality variability as it was injected into four full-scale ASR facilities. Water quality parameters were analyzed using advanced statistical methods. The results show the variability among parameters, water end use, aquifer characteristics, stormwater quality and how aquifer storage may not alter the stormwater quality variability.

Sheng, Z. 2005. An aquifer storage and recovery system with reclaimed wastewater to preserve native groundwater resources in El Paso, Texas. *Journal of environmental*

***management*, 75(4), 367-377.**

This paper utilizes various source water qualities including treated and untreated fresh water as well as reclaimed wastewater and several storage applications including spreading basins, recharge wells, infiltration galleries, and recharge wells to better understand the impacts on ASR practices. The main focus of the paper was on injecting reclaimed water for groundwater preservation and artificial recharge in El Paso, Texas.

A.2.4 Soil Aquifer Treatment

This section contains publications relevant to SAT, hydraulic loading, infiltration, surface spreading, artificial recharge, indirect potable reuse, and removal efficiencies.

Barry, K. E., Vanderzalm, J. L., Miotliński, K., and Dillon, P. J. 2017. Assessing the impact of recycled water quality and clogging on infiltration rates at a pioneering Soil Aquifer Treatment (SAT) site in Alice Springs, Northern Territory (NT), *Australia. Water*, 9(3), 179.

This study conducted field tests using SAT to better understand the infiltration reduction rates that have been observed during MAR operations. This study focused on SAT treatment that involves a mixture of sediment sizes such as fine- and coarse-grained riverine deposits at a MAR Basin in Australia. The results found that including pretreatment technologies such as filtration and UV disinfection prior to recharge improved the infiltration rates by 40 to 100 percent.

Essandoh, H. M., C. Tizaoui, M. H. Mohamed, G. Amy, and D. Brdjanovic. 2011. Soil aquifer treatment of artificial wastewater under saturated conditions. *Water research*, 45(14), 4211-4226.

This study simulated soil aquifer treatment with artificial reclaimed wastewater in a soil column test to investigate removal rates of dissolved organic carbon (DOC), nitrogen, phosphate, and biochemical and chemical oxygen demand (BOD, COD). Hydraulic loading rates were used to determine the removal rates. The results highlight that at a fixed hydraulic loading rate, there was a decrease in concentration for BOD, nitrogen, and phosphate. The results found that shorter residence times resulted in a greater reduction in concentration for the majority of parameters.

Fox, P., K. Narayanaswamy, A. Genz, and J. E. Drewes. 2001. Water quality transformations during soil aquifer treatment at the Mesa Northwest Water Reclamation Plant, USA. *Water Science and Technology,* 43(10), 343-350.

This paper evaluated water quality transformations during SAT by sampling a groundwater monitoring well network within a reclaimed water plume. Groundwater samples were collected for different traveling times ranging from a few days to greater than five years and were analyzed for organic and inorganic parameters such as DOC. A sulfate tracer test was conducted to better understand how SAT influenced DOC concentrations. The main takeaways include that the DOC concentration in the reclaimed wastewater plume was greater than 50 percent the DOC concentration in drinking water.

Laws, B. V., E. R. Dickenson, T. A. Johnson, S. A. Snyder, and J. E. Drewes. 2011. Attenuation

of contaminants of emerging concern during surface-spreading aquifer recharge. ***Science of the Total Environment*****, 409(6), 1087-1094.**

This study investigated the removal efficacy that SAT had on seventeen contaminants of emerging concern that were detected in a recharge basin. The study looked at the impact of travel time, water quality, and attenuation of the contaminants of emerging concern. The results found that after 60 days of travel time in the recharge basin, 11 of the 17 contaminants of emerging concern were reduced by greater than 80 percent due to SAT.

Masciopinto, C., M. Vurro, V. N. Palmisano, and I. S. Liso. 2017. A suitable tool for sustainable groundwater management. ***Water Resources Management*****, 31(13), 4133-4147.**

This study employed a Decision Support System (DSS) that embraces SAT to design an artificial recharge facility. The DSS tool takes into consideration physical, chemical, and biological processes involved in groundwater recharge. This tool provided useful metrics and recommendations for implementation of groundwater recharge utilizing knowledge-based technology and artificial intelligence.

Pauwels, H., V. Ayraud-Vergnaud, L. Aquilina, and J. Molenat. 2010. The fate of nitrogen and sulfur in hard-rock aquifers as shown by sulfate-isotope tracing. ***Applied Geochemistry*****, 25(1), 105-115.**

This study investigated the efficacy of using stable sulfate- and nitrate- isotope tracers to track the fate and transport of sulfate and nitrate in seven hard-rock aquifers that are impacted by agricultural activity in France. The results indicate that both sulfur and nitrogen were cycled in the soil prior to leaching into the groundwater. The study also looked at how the tracers coupled with denitrification impacted the fractionation, assimilation, and oxidation of pyrite and the salinity of the native groundwater.

Shabani, F., R. Aflaki, T. Minamide, T. Venezia, and M. K. Stenstrom. 2020. Soil aquifer treatment to meet reclaimed water requirements. ***Water Environment Research*****, 92(2), 266-277.**

This study conducted a two and a half year long pilot program that explored SAT as a solution to reduce the cost of indirect potable reuse in Southern California. The pilot testing consisted of six column tests that were injected with tertiary effluent from a local wastewater treatment plant. The key parameters that were used to assess the effectiveness of SAT were dissolved organic carbon, biodegradable organic carbon, total organic carbon, and Nitrosodimethylamine (NDMA) as an indicator. The SAT column tests removed NDMA to non-detect values and found a promising 80 percent reduction of organic carbon. The outputs of this pilot test were used to create a kinetic predicative model for biodegradation for indirect potable reuse applications through SAT.

Sharma, S. K., C. M. Harun, and G. Amy. 2008. Framework for assessment of performance of soil aquifer treatment systems. ***Water Science and Technology*****, 57(6), 941-946.**

This study created a framework for analysis, prediction, and removal of organic matter and other biodegradable trace organics to better understand their behaviors during SAT. The framework included guidelines and recommendations for using different water qualities such as primary, secondary, and tertiary treated wastewater effluent as well as analyzed key metrics including soil type and redox conditions.

Sharma, S. K., M. Hussen, and G. Amy. 2011. Soil aquifer treatment using advanced primary effluent. *Water Science and Technology*, 64(3), 640-646.

This paper furthered the research on the impact of using pretreatment technologies prior to injecting primary effluent for groundwater recharge to prevent clogging through SAT infiltration. The study experimented with laboratory-scale batch and soil column experiments on the following three pretreatment technologies: sedimentation, coagulation, and horizontal roughing filtration. The results found that coagulation was the most effective pretreatment technology and reduced the overall suspended solids in the water, but that sedimentation was the most cost-effective option.

Sharma, S. K., and M. D. Kennedy. 2017. Soil aquifer treatment for wastewater treatment and reuse. *International Biodeterioration & Biodegradation*, 119, 671-677.

This paper summarizes how SAT systems can be an effective strategy to improve the water quality of wastewater effluent and recycled water prior to injection. The study reviewed the removal efficiencies of various design techniques including pre- and post-treatment options with respect to cost using SAT infiltration basins. The study took into consideration the hydrogeological conditions, water quality, organics concentrations, and applied process to compare which treatment technology produced the most compatible water quality of the injected water.

A.3 Recharge Water Chemistry

A.3.1 Groundwater Recharge and Reactive Transport Models

This section contains publications relevant to groundwater recharge, reactive transport models, tracer studies, numerical models, and geochemical modeling.

Appelo, C. A. J., and W. W. J. M. De Vet. 2003. Modeling in situ iron removal from groundwater with trace elements such as As. In Arsenic in Ground Water (pp. 381-401). *Springer*, Boston, MA.

In situ iron removal from groundwater may be induced by the cyclical injection of oxygenated water. The efficiency of this process is measured by the ratio of retardations of oxygen during injection and iron during pumping. The PHREEQC hydrogeochemical transport model was used to simulate the first 7 cycles of an in-situ iron removal project in the Netherlands and ion concentration changes are discussed in detail.

Bachtouli, S., and J. C. Comte. 2019. Regional-Scale Analysis of the Effect of Managed Aquifer Recharge on Saltwater Intrusion in Irrigated Coastal Aquifers: Long-Term Groundwater Observations and Model Simulations in NE Tunisia. *Journal of Coastal Research*, 35(1), 91-109.

This study used 50 years of groundwater data specifically groundwater head and salinity records to create a three-dimensional numerical groundwater model for the Korba coastal aquifer in Tunisia. MAR has been in place in the Korba aquifer since 1990 to mitigate the lateral saltwater intrusion, salinization due to irrigation, and groundwater depletion. This model was used to investigate the impact of MAR operations on the spatiotemporal dynamics of groundwater salinization. The model results concluded that the two main contributors to groundwater salinization was indeed from lateral seawater intrusion from the coast and shallow infiltration of evapo-concentrated saline irrigation and that MAR operations helped equilibrate the aquifer.

Brown, C. J., and P. E. Misut. 2010. Aquifer geochemistry at potential aquifer storage and recovery sites in coastal plain aquifers in the New York City area, USA. *Applied geochemistry*, 25(9), 1431-1452.

This study created an extensive three-dimensional reactive solute transport model to look at the effects of injecting New York City's oxic drinking water supply into an anoxic coastal aquifer for a potential ASR site. The New York coastal aquifer is from the Cretaceous era and contains naturally occurring pyrite, goethite, siderite, lignite, and other trace metals like iron. The model evaluated metals mobilization and precipitation, aquifer chemistry, injectate variability, hydraulic issues due to injection, and conducted a sensitivity analysis. The results provided several key findings indicating that ASR can be a cost-effective way to store New York's drinking water supply, stabilize pyrite bearing minerals, and reduce ambient iron concentrations in the groundwater.

Clark, J. F., G. B. Hudson, M. L. Davisson, G. Woodside, and R. Herndon. 2004. Geochemical imaging of flow near an artificial recharge facility, Orange County, California. *Groundwater*, 42(2), 167-174.

This study utilized a series of tracers including geochemical tracer with stable isotope water, tritium/helium-3 dating, and deliberate gas tracer to analyze the water dynamics at a groundwater spreading basin in Southern California. The tracers were followed for two years in the groundwater which allowed the researchers to characterize the subsurface flow patterns and flow times. The results showed the variation in horizontal groundwater velocities and leading-edge velocities and their respective impacts on the transport of microbes and other containments.

Fakhreddine, Sarah, Henning Prommer, Steven M. Gorelick, Jason Dadakis, and Scott Fendorf. Controlling arsenic mobilization during managed aquifer recharge: The role of sediment heterogeneity. *Environmental science & technology* 54.14 (2020): 8728-8738.

This paper investigates the causal mechanisms of arsenic release during MAR injection using reactive transport modeling coupled with aquifer analyses and measured water chemistry. The retention or release of arsenic is affected by the sediment geochemical heterogeneity of the aquifer.

Marston, T. M., and V. M. Heilweil. 2012. Numerical simulation of groundwater movement and managed aquifer recharge from Sand Hollow Reservoir, Hurricane Bench area, Washington County, Utah. US Department of the Interior, US Geological Survey.

The USGS developed a numerical groundwater flow model to simulate groundwater flow and recharge movement in the Hurricane Bench area and the Sand Hollow Reservoir whose primary use is for MAR through the groundwater system. The numerical model was calibrated for both steady state and transient conditions from data from 1975, and 1975 to 2009, respectively. The model simulated natural infiltration of precipitation and infiltration of MAR from the reservoir. The model results were used to better understand the groundwater age, transport of flow, and time considerations for MAR.

Mirecki, J. E. 2006. Geochemical models of water-quality changes during aquifer storage recovery (ASR) cycle tests, Phase 1: Geochemical models using existing data (No. ERDC/EL-TR-06-8). Engineer Research and Development Center Cicksburg MS Environmental Lab.

This study used water quality data from three different ASR sites in Florida to develop geochemical models to better understand ASR operations. The main modeling objectives aimed to better understand the events that take place in ASR cycle testing including: evaluating the groundwater mixing between the native aquifer and the injected/recharged water, understanding the fate, transport, and controls of arsenic, and analyzing the geochemical reactions that occur during the aquifer storage phase. This study also developed an inverse geochemical model to better simulate the redox reactions that take place with arsenic mobility. The results found that existing cycle test data are insufficient to be solely used to quantitatively develop numerical models for groundwater recharge.

A.3.2 Disinfection Types, Residuals, and Byproducts

This section contains publications relevant to types and impact of disinfection byproducts, MAR, water quality considerations, AWT treatment impacts, dissolved organic matter, groundwater management, and contaminants of emerging concern.

Drewes, J. E., C. Hoppe, and T. Jennings. 2006. Fate and transport of N‐nitrosamines under conditions simulating full‐scale groundwater recharge operations. *Water Environment Research*, 78(13), 2466-2473.

This study used laboratory-scale soil column experiments and a full-scale riverbank filtration groundwater monitoring system to investigate the hydrodynamic mechanisms that influence the attenuation of seven N-nitrosamine disinfection byproducts at environmental concentrations under MAR operations. The findings indicate that the seven compounds are biodegradable under both oxic and anoxic redox conditions and that complete removal of the compounds can be observed in the presence of an adapted bio-community.

Hübner, U., S. Kuhnt, M. Jekel, and J. E. Drewes. 2016. Fate of bulk organic carbon and bromate during indirect water reuse involving ozone and subsequent aquifer recharge. *Journal of Water Reuse and Desalination*, 6(3), 413-420.

This study evaluated the removal of DOC and the formation and stability of disinfection byproducts through a series of long-term column testing using ozonated secondary effluent water that is used for MAR. The results indicate that pre-ozonation is an effective strategy to remove DOC such that removal efficiencies increased by 20 percent without pretreatment and doubled to 40 percent after ozonation. Bromate concentrations decreased under anoxic conditions and no significant removal was observed under oxic infiltration.

Landmeyer, J. E., P. M. Bradley, and J. M. Thomas. 2000. Biodegradation of disinfection

byproducts as a potential removal process during aquifer storage recovery 1. *JAWRA Journal of the American Water Resources Association*, 36(4), 861-867.

This study investigated the biodegradation of disinfection byproducts (DBPs) as a potential removal process during ASR by injecting treated surface water into an aerobic aquifer system. The DBPs of interest include trihalomethane and haloacetic acid. The study found that under aerobic and anaerobic aquifer conditions there was no significant biodegradation of trihalomethane and chloroform. Conversely, the study found that in the deep aquifer system mineralization of haloacetic acid occurred on the range of 16 to 27 percent. These findings suggest that trihalomethane DBPs, especially chloroform, are more persistent in groundwater recharge and thus their concentrations should be monitored and minimized prior to injection.

Leenheer, J. A., C. E. Rostad, L. B. Barber, R. A. Schroeder, R. Anders, and M. L. Davisson. 2001. Nature and chlorine reactivity of organic constituents from reclaimed water in groundwater, Los Angeles County, California. *Environmental Science & Technology*, 35(19), 3869-3876.

This paper evaluated the reactivity of organic matter with chlorine and disinfection byproducts (DBPs) prior to, during, and post-injection of reclaimed water into the Montebello Forebay spreading basins in Los Angeles, California. The study characterized and utilized dissolved organic matter as in indicator for removal of DBPs. The results indicate that infiltration of reclaimed water did not negatively impact the native groundwater water quality and showed little contamination due to chlorinated DBPs.

Lekkerkerker-Teunissen, K., Chekol, E. T., Maeng, S. K., Ghebremichael, K., Houtman, C. J., Verliefde, A. R., Q. J. C. Verberk; G. L. Amy; J. C. van Dijk. 2012. Pharmaceutical removal during managed aquifer recharge with pretreatment by advanced oxidation. *Water Science and Technology: Water Supply*, 12(6), 755-767.

This study looked at coupling advanced oxidation processes with MAR to assess the impact of a multi-barrier approach and level of enhanced removal for 14 pharmaceuticals organic micropollutants (OMP). The study utilized laboratory-scale batch reactors to conduct experiments with varied oxidation conditions. The results highlight better removal, from 10 percent to greater than 90 percent OMPs, under oxic conditions than anoxic conditions.

Nalinakumari, B., W. Cha, and P. Fox. 2010. Effects of primary substrate concentration on NDMA transport during simulated aquifer recharge. *Journal of Environmental Engineering*, 136(4), 363-370.

This paper researched the fate and transport of N-Nitrosodimethylamine (NDMA) through two soil column testing systems with differing redox environments to better understand the subsurface transport of the compound during groundwater recharge. The column tests included one aerobic environment and one anoxic environment. Both tests utilized reclaimed water and had varying levels of substrate in this case biodegradable organic carbon. The results found that NDMA removal was similar under anoxic and aerobic conditions but that the effluent concentrations were higher under the anoxic conditions.

O'Leary, D. R., J. A. Izbicki, and L. F. Metzger. 2015. Sources of high-chloride water and

managed aquifer recharge in an alluvial aquifer in California, USA. *Hydrogeology Journal*, 23(7), 1515-1533.

This study identified sources of high chloride water in the alluvial aquifer of the Eastern San Joaquin Subbasin in California and provided a summary of the impacts and mitigation measures that have been put in place to better protect the groundwater water quality. The study monitored eight different recharge wells over a nine-year period and looked at various parameters and processes that could be contributing to this chloride issue. The paper highlighted the most common sources of high chloride water injected into the recharge wells is from irrigation, delta sediments, and deeper aquifers and that it was very common to have more than one source effecting the increased concentrations.

Pavelic, P., B. C. Nicholson, P. J. Dillon, and K. E. Barry. 2005. Fate of disinfection by-products in groundwater during aquifer storage and recovery with reclaimed water. *Journal of Contaminant Hydrology*, 77(1-2), 119-141.

This paper conducted a field-scale study on the fate and transport of trihalomethanes (THMs) and halo acetic acids (HAAs) in an ASR site that injects reclaimed water into an anoxic aquifer in South Australia. The results found that the attenuation of THMs is highly dependent on the geochemical environment and observed half-lives varying from less than one day to 65 days. In contrast, the results highlighted that HAAs attenuated in a much shorter time frame of less than one day. The modeling results highlight these findings as well and suggest that the substantial increases in THMs into the aquifer occur as a result of the chlorinated injected water that still contains residual chlorine and natural organic matter. The paper also recommended that storing water in an anoxic aquifer can improve the water quality relating to the disinfection byproducts.

Pavelic, P., P. J. Dillon, and B. C. Nicholson. 2006. Comparative evaluation of the fate of disinfection byproducts at eight aquifer storage and recovery sites. *Environmental science & technology*, 40(2), 501-508.

This paper provided a comparative assessment of the fate and transport of disinfection byproducts at eight different ASR sites in the United States and Australia. The aquifers had varying hydrological environments, source water compositions, and operating conditions. Analytical techniques including dilution were used to determine the attenuation and formation of trihalomethanes (THMs) in the groundwater following recharge. The findings suggest that there is a high variability of THM attenuation due to the varying geochemical and microbiological conditions in the aquifers. Chloroform was found to be the most persistent disinfection byproduct.

Wang, F., V. Salgado, J. P. Van der Hoek, and D. Van Halem. 2018. Bromate reduction by iron (II) during managed aquifer recharge: a laboratory-scale study. *Water*, 10(4), 370.

This study aimed to fill a literature gap in the research of bromate, a byproduct of ozonation, removal through MAR. This study conducted batch experiments under anoxic conditions to investigate the feasibility of bromate reduction in an iron-reducing aquifer and/or MAR system as well as estimating the potential for nitrate inhibition. The results found that the naturally occurring iron can reduce the bromate concentrations in a MAR system that has relatively low bromate and iron concentrations.

Zhou, Q., S. McCraven, J. Garcia, M. Gasca, T. A. Johnson, and W. E. Motzer. 2009. Field evidence of biodegradation of N-Nitrosodimethylamine (NDMA) in groundwater with incidental and active recycled water recharge. *Water Research*, 43(3), 793-805.

This study sought to provide field evidence of the biodegradation of N-Nitrosodimethylamine (NDMA) in a large-scale groundwater recharge system that utilizes recycled water as the groundwater injectant. The research tracked NDMA concentrations, recycled water quality, and hydrogeologic conditions in 32 production and monitoring wells over a seven-year period. The findings illustrate an overall 90 percent mass reduction of NDMA and an 80 percent recharge mass biodegradation associated with the fate and transport of NDMA occurred in the groundwater system. Therefore, the paper concludes that NDMA can be significantly biodegraded in large groundwater systems.

A.3.3 Water Quality Targets

This section contains publications relevant to water quality targets, groundwater age, water chemistry, trace organics, redox conditions, attenuation, MAR, artificial recharge, and contaminant removal.

Bekele, E., S. Toze, B. Patterson, and S. Higginson. 2011. Managed aquifer recharge of treated wastewater: Water quality changes resulting from infiltration through the vadose zone. *Water Research*, 45(17), 5764-5772.

This paper performed a 39-month field trial utilizing secondary-treated wastewater effluent as the injectant water at a MAR site to assess the possible water quality improvements because of infiltration in the vadose zone. The research studied the changes in microbiology and chemistry of the groundwater directly below the infiltration location and the recycled water prior to infiltration to better characterize the water quality improvements of infiltration. The results depict that infiltration does provide some level of improvements to the water quality when using recycled water but recommends the addition of pretreatment for further improvements.

Drewes, J. E. 2009. Ground water replenishment with recycled water—water quality improvements during managed aquifer recharge. *Groundwater*, 47(4), 502-505.

This article provides a brief overview of the different types of MAR and a discussion of how treatment requirements may vary by MAR type (i.e., basins, injection wells, etc.) when recharging recycled water. The article focuses on evaluating TOC removal through SAT. The author presents an example of water quality changes during SAT using 3-D fluorescence excitation/emission spectra of water samples collected from a full-scale recharge basin, and associated lysimeter and monitoring well.

Patterson, B. M., M. Shackleton, A. J. Furness, E. Bekele, J. Pearce, K. L. Linge, F. Busetti, T. Spadek, and S. Toze. 2011. Behavior and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. *Journal of Contaminant Hydrology*, 122(1-4), 53-62.

This study investigated the fate and transport of nine trace organic compounds, commonly found in recycled water, during a 1-year long large-scale column experiment to simulate

MAR. The experiments evaluated the level of natural attenuation of the compounds under aerobic and anaerobic environments. The study found varying levels of degradation in the different redox environments such that some compounds favored aerobic conditions over anaerobic conditions and vice versa. The results suggest that natural attenuation of the compounds occurred but may not be enough to fully remove the contaminants to the regulatory limits and therefore, suggest that additional pretreatment prior to MAR.

Valhondo, C., J. Carrera, C. Ayora, I. Tubau, L. Martinez-Landa, K. Nödler, and T. Licha. 2015. Characterizing redox conditions and monitoring attenuation of selected pharmaceuticals during artificial recharge through a reactive layer. *Science of the Total Environment*, 512, 240-250.

This paper investigated the efficacy of a permeable reactive layer, located at the floor of an infiltration basin, to remove four pharmaceutical compounds commonly found in treated wastewater that is used during article recharge. The reactive layer was made up of vegetable compost where the organic matter was substrate, and the layer generated a sequence of redox environments. The layer also contained small amounts of clay and iron which increased the sorption capacity of both anionic and cationic species. The results found that the barrier enhanced the removal of three of the four concentrations, providing a reduction in concentration of 20 percent, 40 percent, and values below the detection limits.

Yuan, J., M. I. Van Dyke, and P. M. Huck. 2017. Identification of critical contaminants in wastewater effluent for managed aquifer recharge. *Chemosphere*, 172, 294-301.

This study developed a multi-criteria approach to identify critical contaminants commonly found in treated wastewater effluent and the associated viable treatment technologies to employ prior to using the water for indirect potable reuse through MAR. The study selected the contaminants that were common in treated wastewater effluent and ones that negatively impact human health or the environment. The study conducted a case study in Canada and utilized existing literature to propose potential recharge water quality targets as well as provide guidance for the successful implementation of MAR projects.

Zhang, H., M. Huo, W. Fan, S. Zhu, Y. Lu, H. Xiong, W. Geng, and Lili Dong. 2018. Water quality variation and hydrogeochemical evolution during artificial groundwater recharge with reclaimed water: laboratory experimental and numerical simulation study. *Arabian Journal of Geosciences*, 11(13), 1-16.

This study paired numerical modeling, hydrogeochemical evolution, and laboratory experiments to study water quality variations resulting from the use of reclaimed wastewater for groundwater recharge. The laboratory-scale experiment involved a one-dimensional column test to evaluate soil soluble species dispersion, adsorption, ion exchange, and chemical reactions between the natural material and the reclaimed water. The paper’s key findings include adsorption and dissolution of minerals in the native soil contribute to the changing metals concentrations during recharge, and biodegradation and soil adsorption trap microbial metabolites and proteins.

A.3.4 Water-Rock Reactions

This section contains publications relevant to water-rock reactions, mineral solution interactions, water quality, and aquifer stability.

Herczeg, A. L., K. J. Rattray, P. J. Dillon, P. Pavelic, and K. E. Barry. 2004. Geochemical processes during five years of aquifer storage recovery. *Ground Water*, 42(3), 438.

> The project conducted a five-year pilot study to focus the on geochemical and isotopic data from three observation wells at an experimental ASR site located in a karstic, confined carbonate aquifer in South Australia. The main objective was to investigate the influence of mineral solution interaction between different water types and the impact on water quality and aquifer stability. The study utilized fiver major injection cycles of injecting stormwater into the brackish aquifer and investigated the oxidation reactions of organic matter and sulfide minerals. The results indicate that the water quality showed no evidence of geochemical reactions during the pumping phase of the project and found the release of aqueous carbon dioxide because of the oxidation reactions.

Price, R. E., and T. Pichler. 2006. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water-rock interaction. *Chemical Geology*, 228(1-3), 44-56.

> This paper investigated the impact of arsenic release from cycle testing during ASR from a limestone aquifer in Florida. The study detailed mineralogical and geochemical data from over 300 core samples to determine the abundance and mineralogical association of arsenic. Targeted samples were also collected and analyzed for organic material, hydrous ferric oxide, pyrite, phosphate minerals and clays to allow for more in-depth lithological understanding. The results highlight that recharge water containing high DO concentrations can recover arsenic even when the native groundwater and aquifer matric have observed low concentrations of arsenic.

A.4 Overview of the Annotated Bibliography

No.	Publication	Key Words
A.1 →Aquifer Considerations and Mitigation Measures		
A.1.1 →Clay Dispersion, Clogging, and Stability		
1	Brown, D. L., and W. D. Silvey. 1977. Artificial Recharge to a Freshwater-Sensitive Brackish Water Sand Aquifer, Norfolk, Virginia (Vol. 939). US Government Printing Office.	Artificial recharge, brackish water, sand aquifer, clay dispersion, USGS
2	Dillon, P., P. Pavelic, G. Massmann, K. Barry, and R. Correll. 2001. Enhancement of the membrane filtration index (MFI) method for determining the clogging potential of turbid urban stormwater and reclaimed water used for aquifer storage and recovery. Desalination, 140(2), 153-165.	ASR, MFI, clogging, artificial recharge, water reuse

No.	Publication	Key Words
3	Frenkel, H., J. O. Goertzen, and J. D Rhoades. 1978. Effects of clay type and content, exchangeable sodium percentage, and electrolyte concentration on clay dispersion and soil hydraulic conductivity. Soil Science Society of America Journal, 42(1), 32-39.	Hydraulic conductivity, clay dispersion, sodic soils, exchangeable sodium, water quality
4	Himes, R. E., E. F. Vinson, and D. E. Simon. 1989. Clay stabilization in low-permeability formations. In SPE Production Operations Symposium. Society of Petroleum Engineers. January.	Clay stabilizers, permeability, cationic organic polymers
5	Jeong, H. Y., S. C. Jun, J. Y. Cheon, and M. Park. 2018. A review on clogging mechanisms and managements in aquifer storage and recovery (ASR) applications. Geosciences Journal, 22(4), 667-679.	Artificial recharge, ASR, rehabilitation, injection wells, clogging mechanisms
6	Katzer, T., and K. Brothers. 1989. Artificial recharge in Las Vegas Valley, Clark County, Nevada. Groundwater, 27(1), 50-56.	Artificial recharge, water chemistry, permeability, clogging
7	McNab Jr., W. W., M. J. Singleton, J. E. Moran, and B. K. Esser. 2009. Ion exchange and trace element surface complexation reactions associated with applied recharge of low-TDS water in the San Joaquin Valley, California. Applied Geochemistry, 24(1), 129-137.	Ion exchange, isotope data, tracer study, groundwater age, geochemical modeling, recharge
8	Mohan, K. K., and H. S. Fogler. 1997. Colloidally induced smectitic fines migration: existence of microquakes. AIChE journal, 43(3), 565-576.	Permeability reduction, smectitic fines, swelling, porous media
9	Monaghan, P. H., R. A. Salathiel, B. E. Morgan, and A. D. Kaiser Jr. 1959. Laboratory studies of formation damage in sands containing clays. Transactions of the AIME, 216(01), 209-215.	Formation damage, permeability, clay swelling, clay dispersion
10	Olsthoorn, T. N. 1982. The clogging of recharge wells, main subjects (p. 72). Keuringsinstituut voor Waterleiding Artikelen, KIWA, nv.	Clogging, injection wells, recharge, well design
11	Page, D., K. Miotliński, P. Dillon, R. Taylor, S. Wakelin, K. Levett, Karen Berry, and P. Pavelic. 2011. Water quality requirements for sustaining aquifer storage and recovery operations in a low permeability fractured rock aquifer. Journal of environmental management, 92(10), 2410-2418.	ASR, well clogging, stormwater treatment, stormwater management
12	Page, D., J. Vanderzalm, K. Miotliński, K. Barry, P. Dillon, K. Lawrie, and R. S. Brodie. 2014. Determining treatment requirements for turbid river water to avoid clogging of aquifer storage and recovery wells in siliceous alluvium. Water research, 66, 99-110.	ASR, MAR, well injection, well clogging
13	Pavelic, P., P. J. Dillon, K. E. Barry, J. L. Vanderzalm, R. L. Correll, and S. M. Rinck-Pfeiffer. 2007. Water quality effects on clogging rates during reclaimed water ASR in a carbonate aquifer. Journal of Hydrology, 334(1-2), 1-16.	Artificial recharge, injection, filtrations, biofilms, clogging, carbonate aquifer
14	Reed, M. G. 1972. Stabilization of formation clays with hydroxy-aluminum solutions. Journal of Petroleum Technology, 24(07), 860-864.	Clay stabilizers, clay formation, hydroxy-aluminum solution, permeability

No.	Publication	Key Words
15	Stuyfzand, P. J., and J. Osma. 2019. Clogging issues with aquifer storage and recovery of reclaimed water in the brackish Werribee aquifer, Melbourne, Australia. Water, 11(9), 1807.	ASR, well clogging, recycled water, geochemical analysis, filtration, biofouling, risk management
16	Xia, L., Z. Gao, X. Zheng, and J. Wei. (2018). Impact of recharge water temperature on bioclogging during managed aquifer recharge: a laboratory study. Hydrogeology Journal, 26(7), 2173-2187.	Artificial recharge, bioclogging, temperature, extracellular polymeric substances, MAR
A.1.2 →Hydrogeochemical and Hydrological Considerations		
17	Abdelshafy, M., M. Saber, A. Abdelhaleem, S. M. Abdelrazek, and E. M. Seleem. 2019. Hydrogeochemical processes and evaluation of groundwater aquifer at Sohag City, Egypt. Scientific African, 6, e00196.	Groundwater quality, hydrogeochemical modeling, PHEARQC model, Egypt
18	Antoniou, E. A., B. M. Van Breukelen, B. Putters, and P. J. Stuyfzand. 2012. Hydrogeochemical patterns, processes and mass transfers during aquifer storage and recovery (ASR) in an anoxic sandy aquifer. Applied geochemistry, 27(12), 2435-2452.	ASR, anoxic sand aquifer, hydrogeochemical processes, mobilization, injection, leaching
19	Clark, J. F., S. H. Urióstegui, R. K. Bibby, B. K. Esser, and G. Tredoux. 2016. Quantifying apparent groundwater ages near managed aquifer recharge operations using radio-sulfur (35S) as an intrinsic tracer. Water, 8(11), 474.	MAR, retention time, hydrologic tracer, radio-sulfur (^{35}S)
20	De Vries, J. J., and I. Simmers. 2002. Groundwater recharge: an overview of processes and challenges. Hydrogeology Journal, 10(1), 5-17.	Groundwater recharge, semi-arid region, recharge flux rates, vadose zone
21	Vanderzalm, J. L., D. W. Page, K. E. Barry, and P. J. Dillon. 2010. A comparison of the geochemical response to different managed aquifer recharge operations for injection of urban stormwater in a carbonate aquifer. Applied Geochemistry, 25(9), 1350-1360.	MAR, geochemical, stormwater, carbonate aquifer, calcite dissolution
22	Ye, X., R. Cui, X. Du, S. Ma, J. Zhao, Y. Lu, and Y. Wan. (2019). Mechanism of suspended kaolinite particle clogging in porous media during managed aquifer recharge. Groundwater, 57(5), 764-771.	MAR, porous media, particle clogging, kaolinite
A.1.3 →Lithological Profiling		
23	Descourvières, C., N. Hartog, B. M. Patterson, C. Oldham, and H. Prommer. (2010). Geochemical controls on sediment reactivity and buffering processes in a heterogeneous aquifer. Applied Geochemistry, 25(2), 261-275.	Injection, recovery, water-sediment reactions, heterogeneous aquifer, hydrogeochemical modeling
24	Hewitt, C. H. (1963). Analytical techniques for recognizing water-sensitive reservoir rocks. Journal of Petroleum Technology, 15(08), 813-818.	Permeability, infiltration, reservoir rocks, water

No.	Publication	Key Words
		sensitivity, physical swelling, x-ray diffractions
A.1.4 →Metals Mobilization		
25	Antoniou, E. A., P. J. Stuyfzand, and B. M. van Breukelen. (2013). Reactive transport modeling of an aquifer storage and recovery (ASR) pilot to assess long-term water quality improvements and potential solutions. Applied geochemistry, 35, 173-186.	ASR, reactive transport model, oxygen consumption, leaching, recovered water quality
26	Antoniou, E. A., N. Hartog, B. M. van Breukelen, and P. J. Stuyfzand. (2014). Aquifer pre-oxidation using permanganate to mitigate water quality deterioration during aquifer storage and recovery. Applied geochemistry, 50, 25-36.	ASR, pre-oxidation, water quality, permanganate, ferrous iron, pretreatment
27	Antoniou, E. A., B. M. van Breukelen, and P. J. Stuyfzand. (2015). Optimizing aquifer storage and recovery performance through reactive transport modeling. Applied Geochemistry, 61, 29-40.	ASR, reactive transport model, water quality, anoxic aquifer, varying source waters
28	Blunden, B., and B. Indraratna. (2001). Pyrite oxidation model for assessing ground-water management strategies in acid sulfate soils. Journal of Geotechnical and Geoenvironmental Engineering, 127(2), 146-157.	Pyrite oxidation, groundwater management, sulfate soils, vertical oxygen transport
29	Darling, B. K. (2016). Geochemical factors controlling the mobilization of arsenic at an artificial recharge site, Clearwater, Florida. Journal of Contemporary Water Research and Education, 159(1), 105-116.	ASR, artificial recharge, arsenic, oxidation-reduction potential, oxidative dissolution
30	Fakhreddine, S., J. Dittmar, D. Phipps, J. Dadakis, and S. Fendorf. (2015). Geochemical triggers of arsenic mobilization during managed aquifer recharge. Environmental science & technology, 49(13), 7802-7809.	MAR, arsenic mobilization, trace metals, shallow aquifer, batch and column experiments
31	Hallberg, R. O., and R. Martinell. (1976). Vyredox—in situ purification of ground water. Groundwater, 14(2), 88-93.	Groundwater, iron, manganese, oxidation, Vyredox method, clogging
32	Jin, J., A. R. Zimmerman, S. B. Norton, M. D. Annable, and W. G. Harris. (2016). Arsenic release from Floridan Aquifer rock during incubations simulating aquifer storage and recovery operations. Science of The Total Environment, 551, 238-245.	Arsenic, dissolved organic matter, ASR, groundwater, carbonate rocks, oxidation
33	Jones, G. W. (2015). Investigation of the Mechanisms for Mobilization of Arsenic in Two ASR Systems in Southwest Central Florida.	Arsenic mobility, pyrite stability, ASR, groundwater, limestone, storage-zone
34	Mettler, E., M. Abdelmoula, E. Hoehn, R. Schoenenberger, P. Weidler, and U. Von Gunten. (2001). Characterization of iron and manganese precipitates from an in-situ ground water treatment plant. Ground Water Monitoring and Remediation, 39(6), 921-30.	Groundwater treatment, iron, manganese, precipitation zone, x-ray diffraction

No.	Publication	Key Words
35	Mirecki, J. E., M. W. Bennett, and M. C. López-Baláez. (2013). Arsenic control during aquifer storage recovery cycle tests in the Floridan Aquifer. Groundwater, 51(4), 539-549.	ASR, arsenic sequestration, pyrite oxidation, recovered water
36	Neil, C. W., Y. J. Yang, and Y. S. Jun. (2012). Arsenic mobilization and attenuation by mineral–water interactions: implications for managed aquifer recharge. Journal of Environmental Monitoring, 14(7), 1772-1788.	MAR, arsenic mobilization and attenuation, water-rock reactions, physiochemical processes
37	Neil, C. W., Y. J. Yang, D. Schupp, and Y. S. Jun. (2014). Water chemistry impacts on arsenic mobilization from arsenopyrite dissolution and secondary mineral precipitation: implications for managed aquifer recharge. Environmental science & technology, 48(8), 4395-4405.	MAR, arsenic mobilization, arsenopyrite dissolution, secondary wastewater effluent
38	Neil, C. W. (2015). Understanding the Nano- and Macroscale Processes Impacting Arsenic Mobilization during managed aquifer recharge using Reclaimed Wastewater.	MAR, arsenic mobilization, reclaimed wastewater, reactive transport model
39	Neil, C. W., M. J. Todd, and Y. J. Yang. (2018). Improving arsenopyrite oxidation rate laws: implications for arsenic mobilization during aquifer storage and recovery (ASR). Environmental geochemistry and health, 40(6), 2453-2464.	ASR, arsenic mobilization, arsenopyrite, groundwater, rate law, oxidation
40	Norton, S. B. (2011). Evaluating trace metal mobilization during managed aquifer recharge (Doctoral dissertation, University of Florida).	Trace metal mobilization, MAR, core preservation, degasification pilot test, column experiment, reactive transport model
41	Prommer, H., J. Sun, L. Helm, B. Rathi, A. J. Siade, and R. Morris. (2018). Deoxygenation prevents arsenic mobilization during deepwell injection into sulfide-bearing aquifers. Environmental Science and Technology, 52(23), 13801-13810.	Deep well injection, sulfide-bearing aquifer, deoxygenation, arsenic mobilization, recovery cycles
42	Stolze, L., D. Zhang, H. Guo, and M. Rolle. (2019). Model-based interpretation of groundwater arsenic mobility during in situ reductive transformation of ferrihydrite. Environmental science & technology, 53(12), 6845-6854.	Groundwater, arsenic mobility, reductive transformation, ferrihydrite, iron cycling, geochemical processes
43	Sun, J., H. Prommer, A. J. Siade, S. N. Chillrud, B. J. Mailloux, and B. C. Bostick. (2018). Model-based analysis of arsenic immobilization via iron mineral transformation under advective flows. Environmental science & technology, 52(16), 9243-9253.	Arsenic immobilization, iron mineral transformation, advective flow, aquifer injection
44	Vanderzalm, J. L., P. J. Dillon, K. E. Barry, K. Miotliński, J. K. Kirby, and C. L. G. La Salle. (2011). Arsenic mobility and impact on recovered water quality during aquifer storage and recovery using reclaimed water in a carbonate aquifer. Applied Geochemistry, 26(12), 1946-1955.	ASR, arsenic mobility, carbonate aquifer, reclaimed wastewater, attenuation

No.	Publication	Key Words
45	Wallis, I., H. Prommer, C. T. Simmons, V. Post, and P. J. Stuyfzand. (2010). Evaluation of conceptual and numerical models for arsenic mobilization and attenuation during managed aquifer recharge. Environmental science & technology, 44(13), 5035-5041.	MAR, arsenic attenuation, arsenic mobilization, numerical model, nonreactive transport model
46	Wu, X., B. Bowers, D. Kim, B. Lee, and Y. S. Jun. (2019). Dissolved organic matter affects arsenic mobility and iron (III)(hydr) oxide formation: implications for managed aquifer recharge. Environmental science & technology, 53(24), 14357-14367.	MAR, dissolved organic matter, arsenic mobility, iron formations, bench-scale study
A.1.5 →Organics		
47	Craig, L., J. M. Bahr, and E. E. Roden. (2010). Localized zones of denitrification in a floodplain aquifer in southern Wisconsin, USA. Hydrogeology journal, 18(8), 1867-1879.	Denitrification, hydrogeology, microbial processes, nitrate, ferrous iron, groundwater
48	Linlin, W., Z. Xuan, and Z. Meng. (2011). Transformation of dissolved organic matter in a novel groundwater recharge system with reclaimed water. Water environment research, 83(12), 2140-2147.	Reclaimed water, groundwater recharge, dissolved organic matter, fluorescence spectroscopy, molecular weight distribution
49	Niinikoski, P., S. Saraperä, N. Hendriksson, and J. A. Karhu. (2016). Geochemical and flow modelling as tools in monitoring managed aquifer recharge. Applied Geochemistry, 74, 33-43.	MAR, geochemical modeling, water purification, isotopes, dissolved organic carbon, dissolved inorganic carbon
50	Rauch-Williams, T., C. Hoppe-Jones, and J. E. Drewes. (2010). The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge. Water research, 44(2), 449-460.	Groundwater recharge, MAR, trace organic chemicals, effluent organic matter, riverbank filtration, biotransformation
51	Vanderzalm, J. L., C. L. G. La Salle, and P. J. Dillon. (2006). Fate of organic matter during aquifer storage and recovery (ASR) of reclaimed water in a carbonate aquifer. Applied Geochemistry, 21(7), 1204-1215.	ASR, carbonate aquifer, reclaimed water, organic matter, fate and transport, redox processes
52	Wiese, B., G. Massmann, M. Jekel, T. Heberer, U. Dünnbier, D. Orlikowski, and G. Grützmacher. (2011). Removal kinetics of organic compounds and sum parameters under field conditions for managed aquifer recharge. Water Research, 45(16), 4939-4950.	Bank filtration, kinetics, trace organics, residual concentrations, MAR, multi-tracer
53	Yoon, M. K., and G. L. Amy. (2015). Reclaimed water quality during simulated ozone-managed aquifer recharge hybrid. Environmental Earth Sciences, 73(12), 7795-7802.	MAR, ozone, trace organic contaminants, water reuse, reclaimed wastewater
A.2 →Managed Aquifer Recharge for Potable Reuse		

No.	Publication	Key Words
A.2.1 → Aquifer Injection		
54	Bral, K., W. Jackson, Y. Sim, and T. Morton. (2005). Innovative Approach for Automating Injection Well Systems, Case Study: Dominguez Gap Seawater Intrusion Barrier in Long Beach, California. 12th Biennial Symposium on the Groundwater Recharge, Tucson, AZ.	Injection well, seawater intrusion barrier, groundwater recharge
55	CH2M HILL Engineers, Inc. (CH2M). (2016). Final Report Sustainable Water Recycling Initiative: Groundwater Injection Hydraulic Feasibility Evaluation (Report No. 1). Hampton Roads Sanitation District.	Water reuse, MAR, reclaimed wastewater, feasibility study, groundwater injection
56	Schmidt, C. M., A. T. Fisher, A. Racz, C. G. Wheat, M. Los Huertos, and B. Lockwood. (2012). Rapid nutrient load reduction during infiltration of managed aquifer recharge in an agricultural groundwater basin: Pajaro Valley, California. Hydrological Processes, 26(15), 2235-2247.	Groundwater recharge, nitrate, denitrification, agriculture, water quality
A.2.2 → Groundwater Management		
57	Bekele, E., D. Page, J. Vanderzalm, A. Kaksonen, and D. Gonzalez. (2018). Water recycling via aquifers for sustainable urban water quality management: Current status, challenges and opportunities. Water, 10(4), 457.	MAR, microbial pathogens, metals mobilization, reclaimed water, water recycling, seawater intrusion
58	Dillon, P., P. Stuyfzand, T. Grischek, M. Lluria, R. D. G. Pyne, R. C. Jain, J. Bear, J. Schwarz, W. Wang, E. Fernandez, C. Stefan, M. Pettenati, J. van der Gun, C. Sprenger, G. Massmann, B. R. Scanlon, J. Xanke, P. Jokela, Y. Zheng, R. Rossetto, M. Shamrukh, P. Pavelic, E. Murray, A. Ross, J. P. Bonilla Valverde, A. Palma Nava, N. Ansems, K. Posavec, K. Ha, R. Martin and M. Sapiano. (2019). Sixty years of global progress in managed aquifer recharge. Hydrogeology journal, 27(1), 1-30.	MAR, artificial recharge, water banking, hydrogeology
59	Hellauer, K., D. Mergel, A. S. Ruhl, J. Filter, U. Hübner, M. Jekel, and J. E. Drewes. (2017). Advancing sequential managed aquifer recharge technology (SMART) using different intermediate oxidation processes. Water, 9(3), 221.	MAR, redox conditions, trace organic chemicals, dissolved organic carbon
60	Page, D., E. Bekele, J. Vanderzalm, and J. Sidhu. (2018). Managed aquifer recharge (MAR) in sustainable urban water management. Water, 10(3), 239.	MAR, stormwater harvesting, water recycling, urban water
61	Smith, R., R. Knight, and S. Fendorf. (2018). Overpumping leads to California groundwater arsenic threat. Nature communications, 9(1), 1-6.	Groundwater, pumping, groundwater management, arsenic, land subsidence
62	Spellman, Frank R. 2017. Land Subsidence Mitigation: Aquifer Recharge Using Treated Wastewater Injection. CRC Press.	Artificial recharge, reclaimed wastewater, arsenic, land subsidence

No.	Publication	Key Words
63	Stuyfzand, P. J., and A. Doomen. (2004). The Dutch experience with MARS (Managed Aquifer Recharge and Storage): a review of facilities, techniques, and tools. KIWA NV, Rijswijk, the Netherlands.	MAR, overview, techniques, models, Netherlands
64	Stuyfzand, P. J. (2016). History of managed aquifer recharge in the Netherlands. Electronic Supplementary Material-Hydrogeology Journal Sixty years of global progress in managed aquifer recharge, 36.	ASR, MAR, groundwater management, urban runoff, Netherlands
65	Thomas, B. F. (2018). Sustainability indices to evaluate groundwater adaptive management: a case study in California (USA) for the Sustainable Groundwater Management Act. Hydrogeology Journal, 27(1), 239-248.	Groundwater management, groundwater monitoring, sustainability, framework
66	Yuan, J., M. I. Van Dyke, and P. M. Huck. (2016). Water reuse through managed aquifer recharge (MAR): assessment of regulations/guidelines and case studies. Water Quality Research Journal of Canada, 51(4), 357-376.	MAR, groundwater, water reuse, regulation, potable water
67	Yuan, J., M. I. Van Dyke, and P. M. Huck. (2019). Selection and evaluation of water pretreatment technologies for managed aquifer recharge (MAR) with reclaimed water. Chemosphere, 236, 124886.	MAR, reclaimed water, critical contaminant, water treatment, sustainability
A.2.3 → Aquifer Storage and Recovery		
68	Bral, Kevin M., and Donald R. Kendall. (2006). The Development and Implementation of Aquifer Storage and Recovery in the North Los Posas Basin, Moorpark, California.	ASR, groundwater management, operation considerations
69	Bral, Kevin, T. Tangsutthinon, and S. Chusanathas. (2015). Demonstration Program to Mitigate Drought and Flooding in the Northern Part of the Chao Phraya River Basin, Thailand Using ASR Methods—Part 2. GEOINDO, 23 Nov. 2015.	Artificial recharge, ASR, Thailand, hydrogeological testing methods
70	Brown, C. J., J. Ward, and J. Mirecki. (2016). A revised brackish water aquifer storage and recovery (ASR) site selection index for water resources management. Water resources management, 30(7), 2465-2481.	ASR, brackish water, performance factors, recovery efficiency, site selection
71	CH2M HILL Engineers, Inc. (CH2M HILL). (2010). Phased implementation of a large-scale aquifer storage and recovery system in San Antonio, Texas, USA. Prepared for Texas Water Development Board, Austin, Texas.	Large-scale ASR, water impoundment, evaporative losses
72	Chinnasamy, C. V., W. C. McIntyre, and D. C. Mays. (2018). Technical and administrative feasibility of alluvial aquifer storage and recovery on the South Platte River of northeastern Colorado. Water Policy, 20(4), 841-854.	ASR, clogging, MAR, reusable effluent, feasibility study, semi-arid,
73	Forghani, A., and R. C. Peralta. (2018). Intelligent performance evaluation of aquifer storage and recovery systems in freshwater aquifers. Journal of Hydrology, 563, 599-608.	ASR, recovery effectiveness, sensitivity analysis, decision support systems, neutral networks

No.	Publication	Key Words
74	Otero, C. L., and B. L. Petri. (2010). Quality of Groundwater at and Near an Aquifer Storage and Recovery Site, Bexar, Atascosa, and Wilson Counties, Texas, June 2004-August 2008. US Department of the Interior, US Geological Survey.	ASR, groundwater quality, USGS, sample collection, pre-injection, post-injection
75	Page, D. W., L. Peeters, J. Vanderzalm, K. Barry, and D. Gonzalez. (2017). Effect of aquifer storage and recovery (ASR) on recovered stormwater quality variability. Water research, 117, 1-8.	MAR, ASR, urban stormwater, natural treatment, groundwater management
76	Sheng, Z. (2005). An aquifer storage and recovery system with reclaimed wastewater to preserve native groundwater resources in El Paso, Texas. Journal of environmental management, 75(4), 367-377.	ASR, groundwater, water quality compatibility, reclaimed wastewater
A.2.4 → Soil Aquifer Treatment		
77	Barry, K. E., J. L. Vanderzalm, K. Miotliński, and P. J. Dillon. (2017). Assessing the impact of recycled water quality and clogging on infiltration rates at a pioneering Soil Aquifer Treatment (SAT) site in Alice Springs, Northern Territory (NT), Australia. Water, 9(3), 179.	SAT, clogging, infiltration rates, MAR, recycled water
78	Essandoh, H. M., C. Tizaoui, M. H. Mohamed, G. Amy, and D. Brdjanovic. (2011). Soil aquifer treatment of artificial wastewater under saturated conditions. Water research, 45(14), 4211-4226.	SAT, chemical oxygen demand, hydraulic loading rate, mass loading rate, removal efficiency, artificial recharge
79	Fox, P., K. Narayanaswamy, A. Genz, and J. E. Drewes. (2001). Water quality transformations during soil aquifer treatment at the Mesa Northwest Water Reclamation Plant, USA. Water Science and Technology, 43(10), 343-350.	SAT, dissolved organic carbon, groundwater, travel time, reclaimed wastewater
80	Laws, B. V., E. R. Dickenson, T. A. Johnson, S. A. Snyder, and J. E. Drewes. (2011). Attenuation of contaminants of emerging concern during surface-spreading aquifer recharge. Science of the Total Environment, 409(6), 1087-1094.	SAT, indirect potable reuse, surface spreading, contaminants of emerging concern
81	Masciopinto, C., M. Vurro, V. N. Palmisano, and I. S. Liso. (2017). A suitable tool for sustainable groundwater management. Water Resources Management, 31(13), 4133-4147.	Artificial recharge, groundwater, artificial intelligence, SAT, recharge plant design, MAR
82	Pauwels, H., V. Ayraud-Vergnaud, Aquilina, L., and Molenat, J. (2010). The fate of nitrogen and sulfur in hard-rock aquifers as shown by sulfate-isotope tracing. Applied Geochemistry, 25(1), 105-115.	Sulfate-isotope tracing, hard-rock aquifer, nitrogen, sulfur, brackish groundwater, mixing
83	Shabani, F., Aflaki, R., Minamide, T., Venezia, T., and Stenstrom, M. K. (2020). Soil aquifer treatment to meet reclaimed water requirements. Water Environment Research, 92(2), 266-277.	Indirect potable reuse, biodegradable dissolved organic carbon, ozonation, reclamation, SAT

No.	Publication	Key Words
84	Sharma, S. K., C. M. Harun, and G. Amy. (2008). Framework for assessment of performance of soil aquifer treatment systems. Water Science and Technology, 57(6), 941-946.	Organic matter, framework, secondary effluent, travel time, SAT
85	Sharma, S. K., M. Hussen, and G. Amy. (2011). Soil aquifer treatment using advanced primary effluent. Water Science and Technology, 64(3), 640-646.	SAT, primary effluent, pretreatment, coagulation, sedimentation, bulk organic matter
86	Sharma, S. K., and M. D. Kennedy. (2017). Soil aquifer treatment for wastewater treatment and reuse. International Biodeterioration & Biodegradation, 119, 671-677.	SAT, water reuse, infiltration basin, pre- and post-treatment, removal efficiency, hybrid system
A.3 →Recharge Water Chemistry		
A.3.1 → Groundwater Recharge and Reactive Transport Model		
87	Appelo, C. A. J., and W. W. J. M. De Vet. (2003). Modeling in situ iron removal from groundwater with trace elements such as As. In Arsenic in Ground Water (pp. 381-401). Springer, Boston, MA.	Groundwater, trace elements, arsenic, injection, oxygenated water, in situ iron removal
88	Bachtouli, S., and J. C. Comte. (2019). Regional-Scale Analysis of the Effect of Managed Aquifer Recharge on Saltwater Intrusion in Irrigated Coastal Aquifers: Long-Term Groundwater Observations and Model Simulations in NE Tunisia. Journal of Coastal Research, 35(1), 91-109.	Groundwater management, irrigated agriculture, MAR, saltwater intrusion
89	Brown, C. J., and P. E. Misut. (2010). Aquifer geochemistry at potential aquifer storage and recovery sites in coastal plain aquifers in the New York City area, USA. Applied geochemistry, 25(9), 1431-1452.	ASR, groundwater injection, oxic water, reactive solute transport model, iron, dissolution
90	Clark, J. F., G. B. Hudson, M. L. Davisson, G. Woodside, and R. Herndon. (2004). Geochemical imaging of flow near an artificial recharge facility, Orange County, California. Groundwater, 42(2), 167-174.	Artificial recharge, geochemical imaging, stable isotopes, tracer study
91	Fakhreddine, Sarah, J. Dittmar, D. Phillips, J. Dadakis, S. Fendorf. Controlling arsenic mobilization during managed aquifer recharge: The role of sediment heterogeneity. Environmental Science and Technology 54.14 (2020): 8728-8738.	MAR, arsenic mobilization, sediment heterogeneity, reactive transport modeling, groundwater injection
92	Marston, T. M., and V. M. Heilweil. (2012). Numerical simulation of groundwater movement and managed aquifer recharge from Sand Hollow Reservoir, Hurricane Bench area, Washington County, Utah. US Department of the Interior, US Geological Survey.	Groundwater modeling, numerical model, calibration, MAR, USGS
93	Mirecki, J. E. (2006). Geochemical models of water-quality changes during aquifer storage recovery (ASR) cycle tests, Phase 1: Geochemical models using existing data (No. ERDC/EL-TR-06-8). Engineer Research and Development Center Cicksburg MS Environmental Lab.	ASR, geochemical model, water quality, recharge, arsenic mobility

No.	Publication	Key Words
A.3.2 → Disinfection Types, Residuals, and Byproducts		
94	Drewes, J. E., C. Hoppe, and T. Jennings. (2006). Fate and transport of N-nitrosamines under conditions simulating full-scale groundwater recharge operations. Water Environment Research, 78(13), 2466-2473.	Groundwater recharge, water reuse, N-Nitrosodimethylamine (NDMA), disinfection byproducts
95	Hübner, U., S. Kuhnt, M. Jekel, and J. E. Drewes. (2016). Fate of bulk organic carbon and bromate during indirect water reuse involving ozone and subsequent aquifer recharge. Journal of Water Reuse and Desalination, 6(3), 413-420.	MAR, ozonation, riverbank filtration, dissolved organic carbon, bromate, water reuse
96	Landmeyer, J. E., P. M. Bradley, and J. M. Thomas. (2000). Biodegradation of disinfection byproducts as a potential removal process during aquifer storage recovery. JAWRA Journal of the American Water Resources Association, 36(4), 861-867.	Biodegradation, ASR, aerobic aquifer, geochemistry, disinfection byproducts, surface water hydrology, water management
97	Leenheer, J. A., C. E. Rostad, L. B. Barber, R. A. Schroeder, R. Anders, and M. L. Davisson. (2001). Nature and chlorine reactivity of organic constituents from reclaimed water in groundwater, Los Angeles County, California. Environmental Science and Technology, 35(19), 3869-3876.	Groundwater, reclaimed water, dissolved organic matter, chlorine reactivity, groundwater age
98	K. Lekkerkerker-Teunissen; E. T. Chekol; S. K. Maeng; K. Ghebremichael; C. J. Houtman; A. R. D. Verliefde; J. Q. J. C. Verberk; G. L. Amy; J. C. van Dijk. (2012). Pharmaceutical removal during managed aquifer recharge with pretreatment by advanced oxidation. Water Science and Technology: Water Supply, 12(6), 755-767.	MAR, drinking water, organic micropollutants, oxic conditions, ozonation, soil passage, pretreatment
99	Nalinakumari, B., W. Cha, and P. Fox. (2010). Effects of primary substrate concentration on NDMA transport during simulated aquifer recharge. Journal of Environmental Engineering, 136(4), 363-370.	Groundwater recharge, aquifer, substrate, biodegradation, water reclamation, NDMA
100	O'Leary, D. R., J. A. Izbicki, and L. F. Metzger. (2015). Sources of high-chloride water and managed aquifer recharge in an alluvial aquifer in California, USA. Hydrogeology Journal, 23(7), 1515-1533.	Groundwater recharge, groundwater management, heterogeneity, water budget, MAR
101	Pavelic, P., B. C. Nicholson, P. J. Dillon, and K. E. Barry. (2005). Fate of disinfection by-products in groundwater during aquifer storage and recovery with reclaimed water. Journal of Contaminant Hydrology, 77(1-2), 119-141.	ASR, groundwater, biodegradation, haloacetic acid, trihalomethanes, reclaimed water
102	Pavelic, P., P. J. Dillon, and B. C. Nicholson. (2006). Comparative evaluation of the fate of disinfection byproducts at eight aquifer storage and recovery sites. Environmental Science and Technology, 40(2), 501-508.	ASR, reclaimed water, attenuation and formation of trihalomethanes, redox conditions, groundwater mixing

No.	Publication	Key Words
103	Wang, F., V. Salgado, J. P. Van der Hoek, and D. Van Halem. (2018). Bromate reduction by iron (II) during managed aquifer recharge: a laboratory-scale study. Water, 10(4), 370.	MAR, iron-reducing zones, ozonation, bromate reduction, drinking water treatment, nitrate
104	Zhou, Q., S. McCraven, J. Garcia, M. Gasca, T. A. Johnson, and W. E. Motzer. (2009). Field evidence of biodegradation of N-Nitrosodimethylamine (NDMA) in groundwater with incidental and active recycled water recharge. Water Research, 43(3), 793-805.	Artificial recharge, groundwater, surface water, photolysis, biodegradation, NDMA
A.3.3 → Water Quality Targets		
105	Bekele, E., S. Toze, B. Patterson, and S. Higginson. (2011). Managed aquifer recharge of treated wastewater: Water quality changes resulting from infiltration through the vadose zone. Water Research, 45(17), 5764-5772.	MAR, wastewater infiltration, natural attenuation processes, reclaimed water
106	Drewes, J. E. (2009). Ground water replenishment with recycled water—water quality improvements during managed aquifer recharge. Groundwater, 47(4), 502-505.	MAR, groundwater, recycled water, water quality, SAT, TOC
107	Patterson, B. M., M. Shackleton, A. J. Furness, E. Bekele, J. Pearce, K. L. Linge, F. Busetti, T. Spadek, S. Toze. (2011). Behavior and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. Journal of Contaminant Hydrology, 122(1-4), 53-62.	MAR, trace organics, biodegradation, retardation, recycled water, aerobic aquifer
108	Valhondo, C., J. Carrera, C. Ayora, I. Tubau, L. Martinez-Landa, K. Nödler, and T. Licha. (2015). Characterizing redox conditions and monitoring attenuation of selected pharmaceuticals during artificial recharge through a reactive layer. Science of the Total Environment, 512, 240-250.	SAT, reactive barrier, redox conditions, contaminant attenuation, artificial recharge, field-scale observations
109	Yuan, J., M. I. Van Dyke, and P. M Huck. (2017). Identification of critical contaminants in wastewater effluent for managed aquifer recharge. Chemosphere, 172, 294-301.	MAR, reclaimed water, wastewater, water reuse, contaminant removal
110	Zhang, H., M. Huo, W. Fan, S. Zhu, Y. Lu, H. Xiong, W. Geng, and L. Dong. (2018). Water quality variation and hydrogeochemical evolution during artificial groundwater recharge with reclaimed water: laboratory experimental and numerical simulation study. Arabian Journal of Geosciences, 11(13), 1-16.	Artificial recharge, reclaimed water, water quality variations, hydrogeochemical evolution, groundwater modeling
A.3.4 → Water-Rock Reactions		
111	Herczeg, A. L., K. J. Rattray, P. J. Dillon, P. Pavelic, and K. E. Barry. 2004. Geochemical processes during five years of aquifer storage recovery. Ground Water, 42(3), 438.	ASR, carbonate aquifer, mineral solution interactions, water quality, aquifer stability
112	Price, R. E., and T. Pichler. 2006. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications	ASR, arsenic, pyrite, limestone, cycle testing

No.	Publication	Key Words
	for arsenic release during water-rock interaction. Chemical Geology, 228(1-3), 44-56.	

Appendix B

Utility Survey

B.1 Approach and Methodology

An extensive utility survey was developed under Task 2 of this project. The primary objective of the survey was to obtain important information relevant to MAR facilities and to gain a deeper understanding for the types of challenges faced and the solutions utilities have developed to overcome these issues. The project team developed a questionnaire in Excel and sectioned it off into five hierarchical topics including *MAR Facility in Operation, MAR Facility in Planning, MAR System Performance, Aquifer Characteristics and Water Quality,* and *MAR Benefits*.

- The *MAR Facility in Operation* section provided details on the overall type of MAR facility, spreading basins, injection wells, monitoring systems, and type of AWT. The information from this section was used to categorize facilities by MAR processes, water quality challenges, and level of AWT.
- The MAR Facility in Planning section provided information on the type of MAR facility that is being considered, identified MAR benefits, supporting feasibility information, pilot testing and/or field investigation specifics. Similar to the MAR Facility in Operations, this section used the same metrics to categorize MAR facilities in the planning stage of the project.
- The MAR System Performance section collected information that helped quantify current MAR system performance with a focus on operational and environmental issues. This section was intended for utilities who are currently operating a MAR facility.
- The Aquifer Characteristics and Water Quality section gathered data to quantify the water quality and aquifer characteristics of the recharge system. The information in this section pertained to the receiving aquifer, the recharge water quality, NGW quality, and migrating recharge in an aquifer from a monitoring well. The utilities were asked to provide relevant water quality data if available. This section was intended for utilities who are currently operating a MAR facility. However, if utilities who were in the planning phase had the requested water quality data, the project team encouraged them to submit it.
- The MAR Benefits section asked for information specific to the recharge benefits observed or quantified at the MAR facility. Facilities in the planning phase identified the potential MAR benefits in the *MAR Facilities in Planning* section.

Utilizing existing industry connections, the project team requested participation from known utilities with MAR facilities in operations as well as utilities in the planning phase of a MAR facility. The survey was distributed to the five utility partners as well as seven other utilities.

Appendix C

Testing the Decision Framework Using Utility Survey Responses

This appendix uses data provided by the project's survey participants to test the Decision Framework tool in solving common geochemical problems encountered during MAR operations. Each section describes a geochemical issue, how to use the appropriate flowchart(s) in approaching and mitigating the problem. Issues chosen for consideration include:

- Basin/well clogging
- Metals mobilization
- Clay dispersion

C.1 Clogging

Physical and geochemical issues represent a significant portion of the mechanisms clogging basins and/or well clogging. Performance losses caused by clogging reduce MAR capacity, while the effort required to maintain the MAR facilities expend significant time and cost. Moreover, clogging issues affect MAR operations over the service life of the facility. The most common clogging mechanisms active in basins and wells include the following:

- Siltation
- Biofouling
- Minerals precipitation
- Air binding

Even the most highly purified recharge contains some amount of TSS that accumulate in the bottom of a basin, well screen slots, the filter pack behind a screen, or fill the open pore space of receiving formations. Furthermore, even though other clogging mechanisms may prove more prevalent, yet TSS continuously accumulates during MAR operations (Figure C-1).

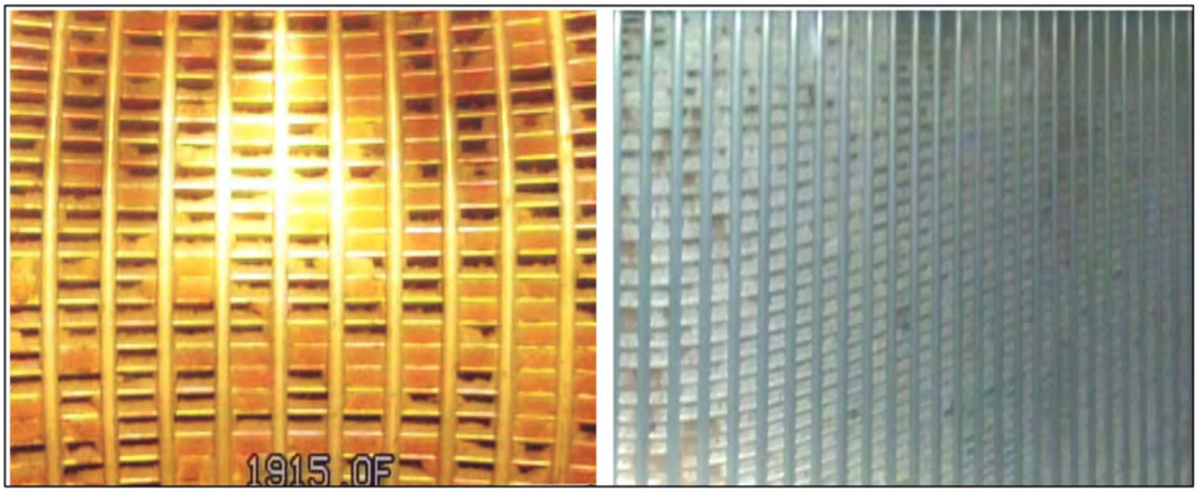


Figure C-1. Examples of Clogging by Siltation in a Screened MAR Well.

In the environments conducive to biological growth, biota-produced film, slime, or filamentous masses can clog basin or wells (Figure C-2). Thus, removing nutrients like TOC, nitrogen-related constituents, and phosphate, if practical, plus disinfection help arrest the growth of biofilms in a MAR facility.

Figure C-2. Examples of Biofouling in Screened MAR Wells.

Mineral precipitation arises as an issue when recharging water containing elevated DO into an aquifer containing elevated concentrations of dissolved metals, most commonly iron (Figure C-3). The mechanism presents the greatest concerns during early MAR operations when precipitates form adjacent to the basin or wellbore. The problem diminishes with time as the recharge front migrates further into the aquifer where surface areas expand geometrically. Building precipitates on reactive minerals in the aquifer matrix represents less of an issue. Reduced metal-bearing minerals typically comprise less than 1 percent of the aquifer mass, and thus, precipitating coatings and surfaces clog negligible pore space in the aquifer.

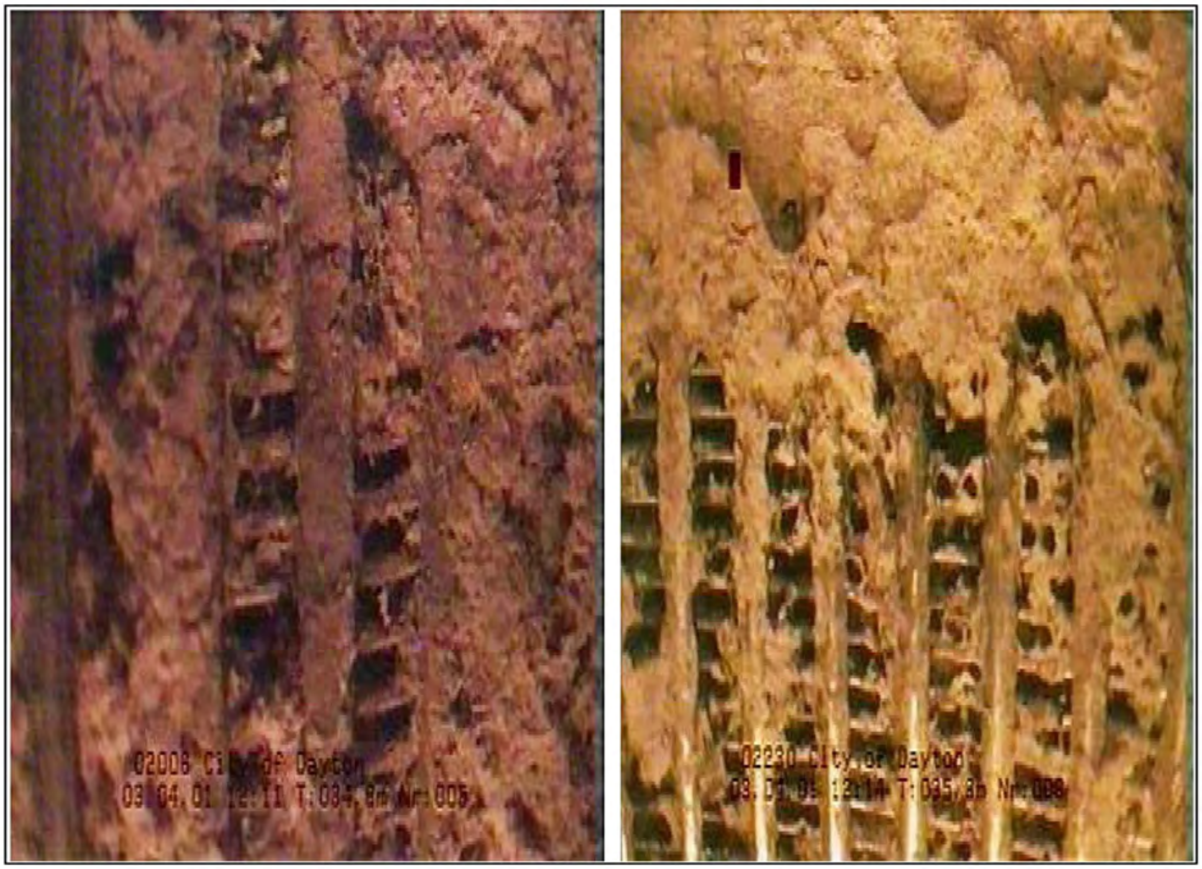


Figure C-3. Examples of Mineral Precipitation in MAR Wells.

Of the listed mechanisms, air binding represents a larger concern for clogging shallow wells or deep wells with a corresponding deeper static water or recharge water levels that extend into the screen or open interval of the well. According to Henry's Law (Langmuir 1997) gas cannot exist as a separate phase in water under the ambient or recharge hydrostatic pressures (1 to 100 bar) encountered in a deep screen assembly. Thus, gases typically dissolve in recharge rather than blocking a well screen or fracture apertures as bubbles. The greatest vulnerability emerges in wells where the static and potentially injection water level falls below the top of the screen.

C.1.1 Path to a Solution

The surveys reveal that utilities operating MAR facilities relying on basins conduct routine maintenance several times annually. These measures include draining, drying and scraping the basin surfaces to remove films of silt, clay and biological matting usually conducted every six months. The effort requires removing the basin from service and letting it dry for several days to weeks. Less frequently, utilities including OCWD and Tucson Water remove surface soils from basin surfaces and replace the material with coarse-grained, well-sorted sand.

Given the small surface area around a MAR wellbore, a clogging area hidden from view, and limited accessibility for cleaning, MAR wells face more challenging issues when clogging than basins. Moreover, routine maintenance measures like backflushing or even periodic non-invasive chemical rehabilitation provide energetically limited options resulting in constrained benefits.

Invasive rehabilitation options work the best for restoring recharge specific capacity (injectivity) but require removing the well from service for several weeks to months and withdrawing downhole equipment before starting rehabilitation activities. Furthermore, invasive rehabilitation for deep wells containing long screens or open areas, cost several hundred thousand dollars to complete, a cost prohibitive factor if required frequently. Most literature (Driscoll 1986; Houben and Trestakis 2007) recommend invasive rehab measures once the specific capacity in production wells declines by 15 to 20 percent. However, utilities can show more leniency regarding the guideline in MAR wells, where constituents in the recharge cause most problems in surficial areas of the wellbore, like the screen face or fracture apertures, and thus, require less energy for removal.

C.1.1.1 Membrane and Bypass Filter Index Testing

Flowcharts addressing clogging in wells (Figures C-4 and C-5) consider both routine and invasive rehab measures. Unlike most geochemical issues which utilities can diagnose in Phases 1 and 2 of the MAR project, because of the lack of recharge properties until construction of the AWT, a utility cannot assess the clogging potential of recharge until Phase 3. A simple approach for periodically assessing the clogging potential of recharge involves running MFI and BFI testing (Figures C-6 and C-7). Ultimately, a permanent MAR facility should contain permanent MFI and BFI stations connected to wellheads or at locations where finished AWT effluent flows through smaller diameter piping like a laboratory.

MFI describes the slope of the line that shows the inverse of the flow rate (Figure C-8) versus the amount of water that passes through a membrane filter containing 0.45 µm pores under constant pressure, standard temperature and filter area (Olsthoorn 1982). Many researchers (Olsthoorn 1982; Hutchinson 1997; Buik and Willemsen 2002; Stuytzand and Osma 2019; Schippers and Verdouw 1980) regard the MFI, referred to in this report as MFIs or MFI indices, as the best parameter to predict the clogging potential of an infiltrating water. Researchers (Hijnen, et al. 1998) set an MFI of 3 sec/L^2 as a threshold for successful long-term MAR operations relatively free of clogging issues. Thus, the Decision Framework process recognizes the MFI threshold as a guide for implementing routine maintenance measures in MAR wells.

Despite the reliance on MFI indices to control the frequency of maintenance measures described here, OCWD successfully runs its MAR well operations employing periodic aggressive invasive rehab measures to maintain injectivity in their wells.

C.1.1.2 Backflushing

One important routine maintenance procedure featured in the Decision Framework flowcharts involves backflushing (Figure C-4). During recharge operations backflushing entails stopping recharge, pumping the well for several minutes according to its depth, pumping rate, and time for water to reach the ground surface from the well's screen or open area. Backflushing removes particulates accumulating in the screen and filter pack since the last backflushing event (Figure C-9). At the completion of backflushing, the well resumes recharging.

Employing backflushing as a maintenance measure requires equipping the MAR well with a pump that produces rates that exceed the recharge rate by 1.5 to 3 times for maximum effectiveness (Stuyfzand and Osma 2019). Also, using backflushing as a maintenance measure requires having a location to dispose of the backflush effluent. At some wells, depending on local hydraulic and regulatory constraints, wells can backflush to storm drains, surface water, local sewer system, or even directly to the AWT influent.

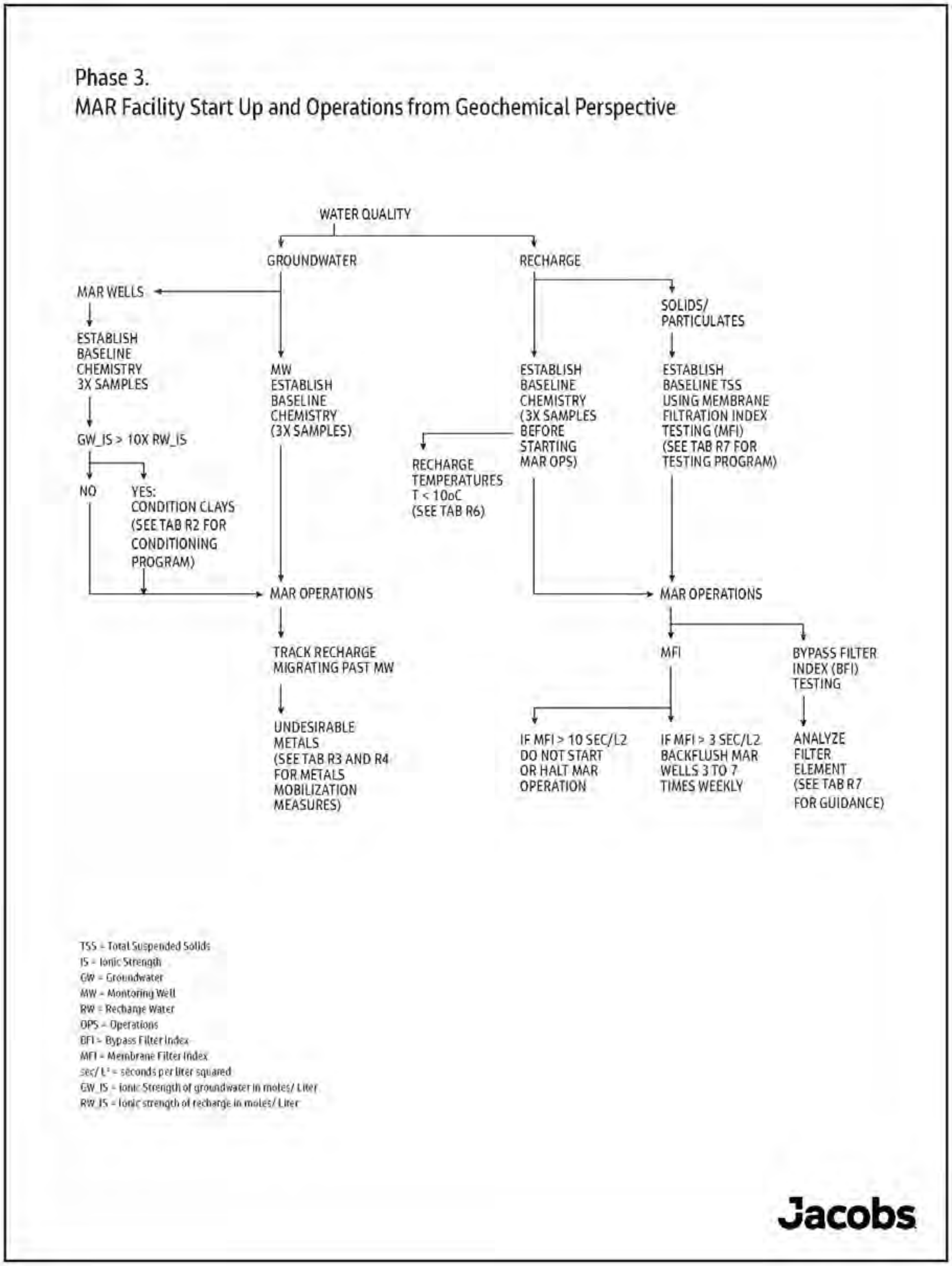


Figure C-4. Decision Framework Flowchart for Phase 3 MAR Startup and Operations.

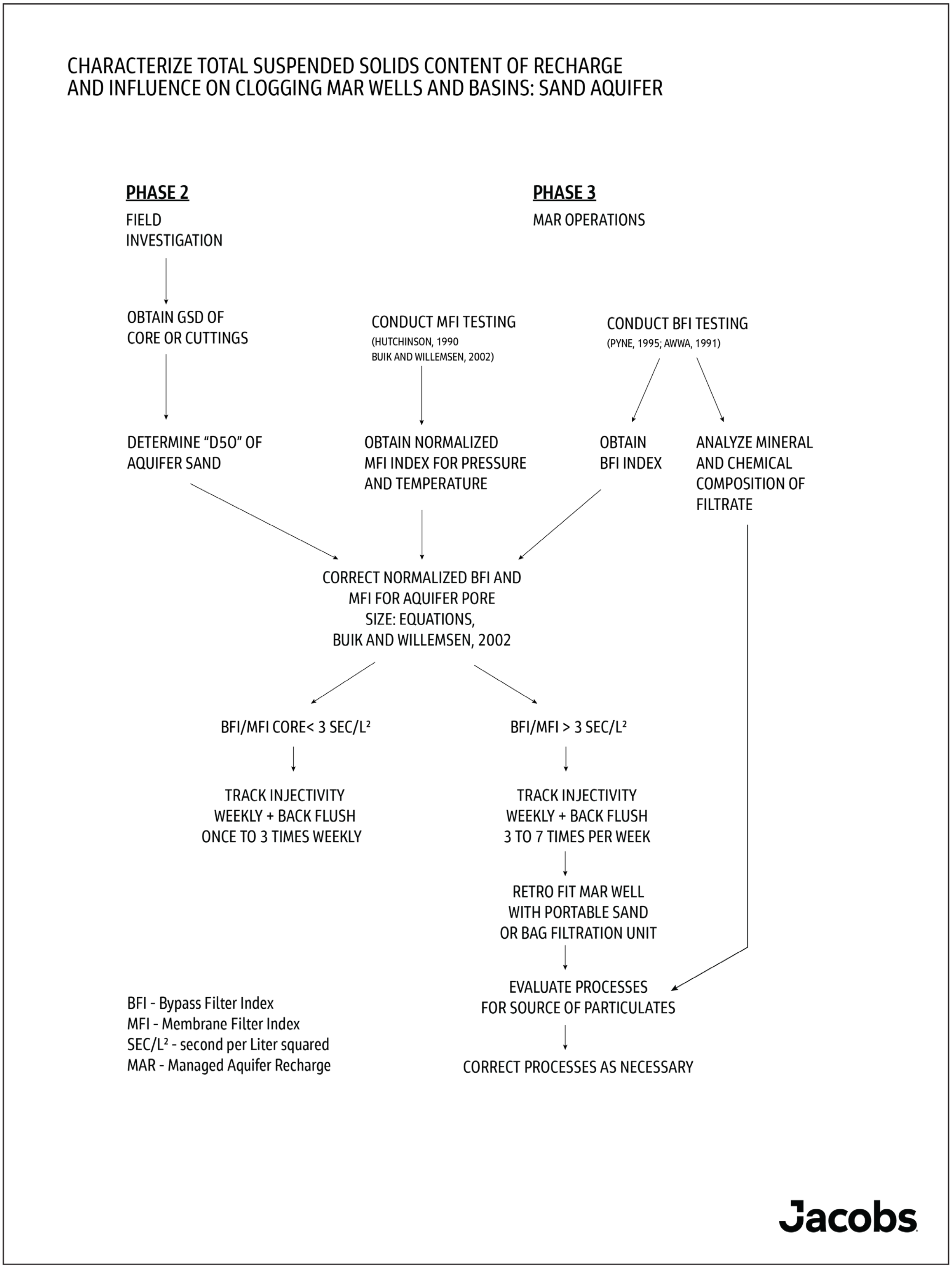


Figure C-5. Decision Framework Flowchart for MFI Testing.

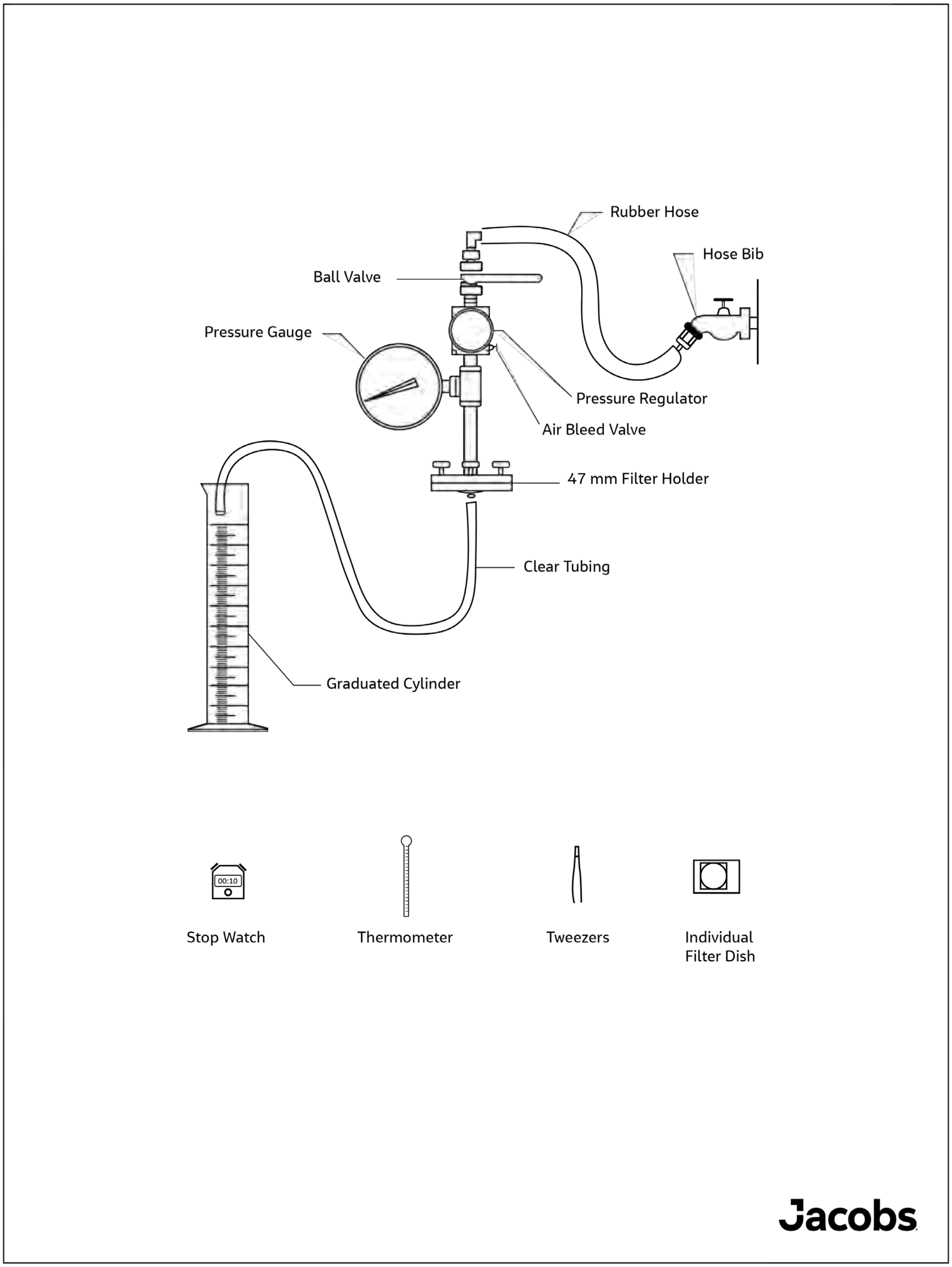
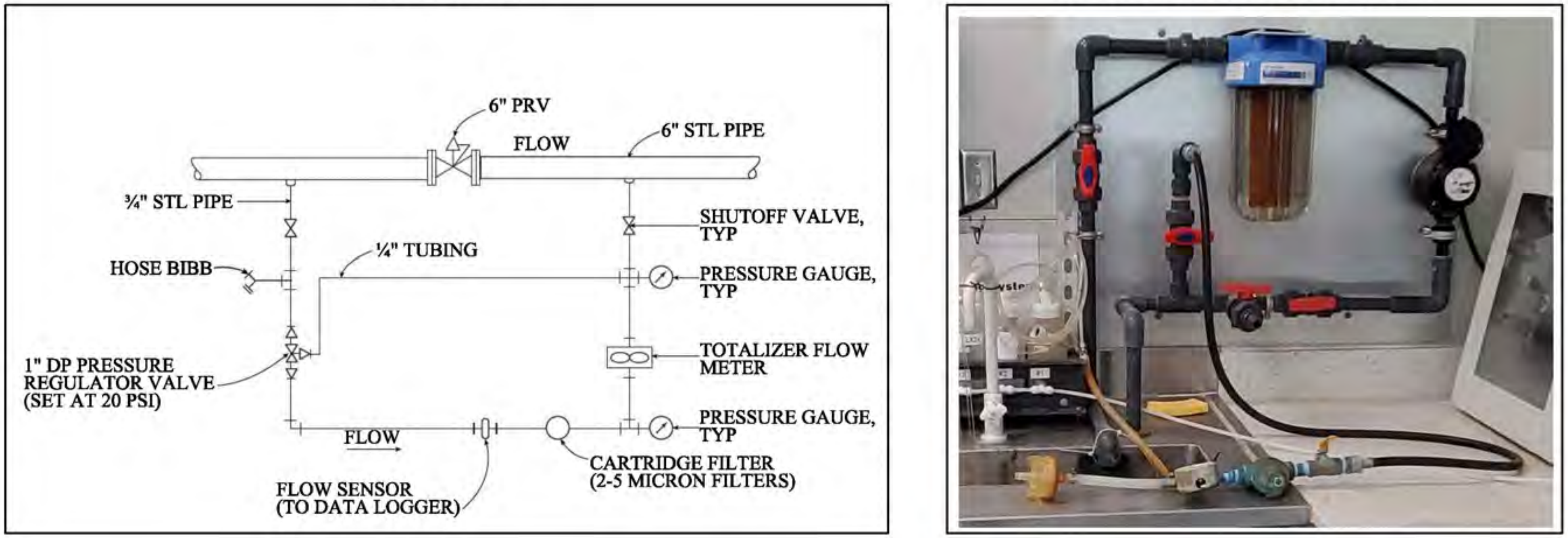


Figure C-6. Illustration of MFI Testing Equipment.



BFI Schematic

BFI Device in MAR Facility Lab

Figure C-7. BFI Schematic and Testing Station in Lab at SRC.

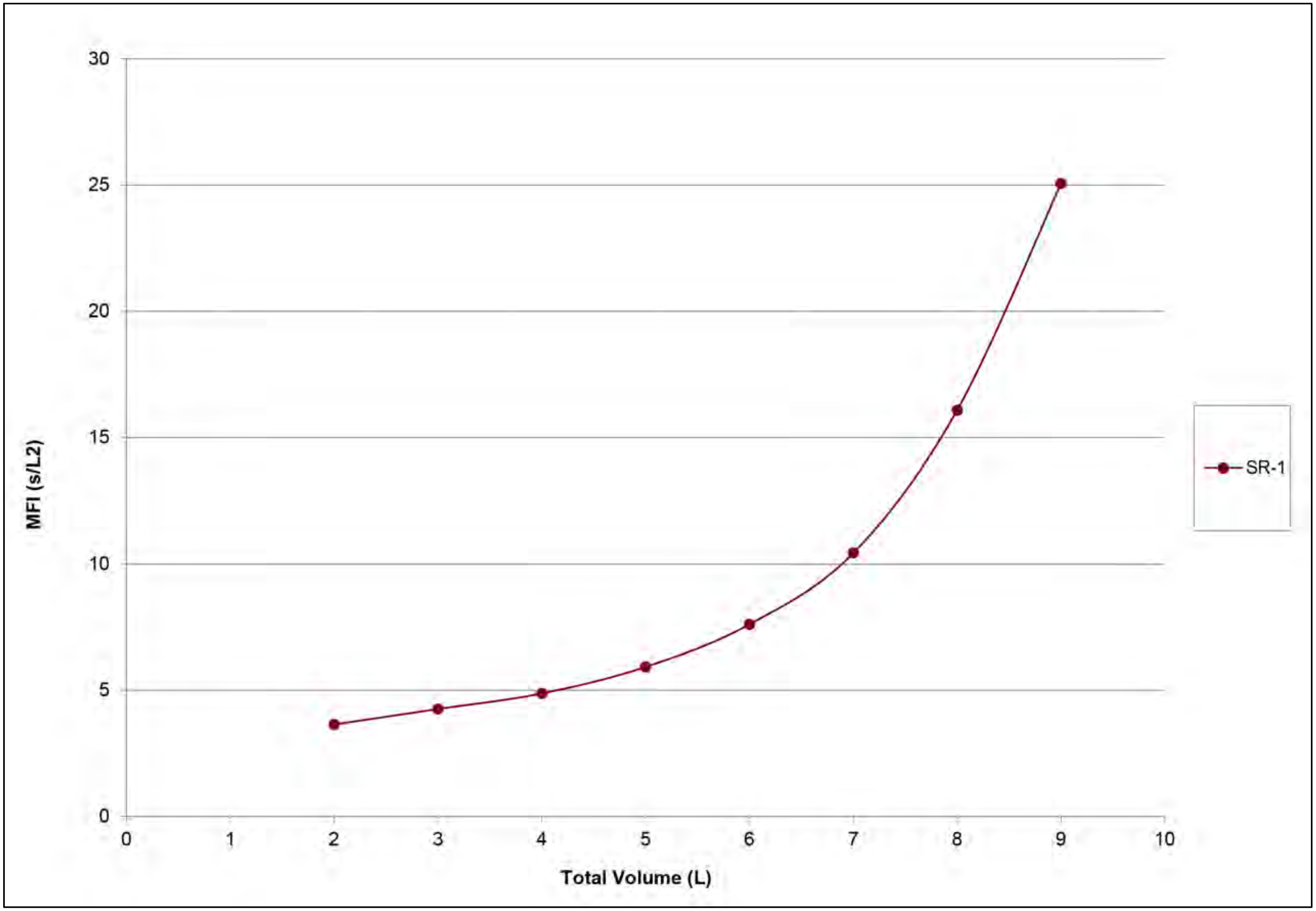


Figure C-8. Example MFI Data Curve.

Figure C-9. Example of Backflushing Discharge.

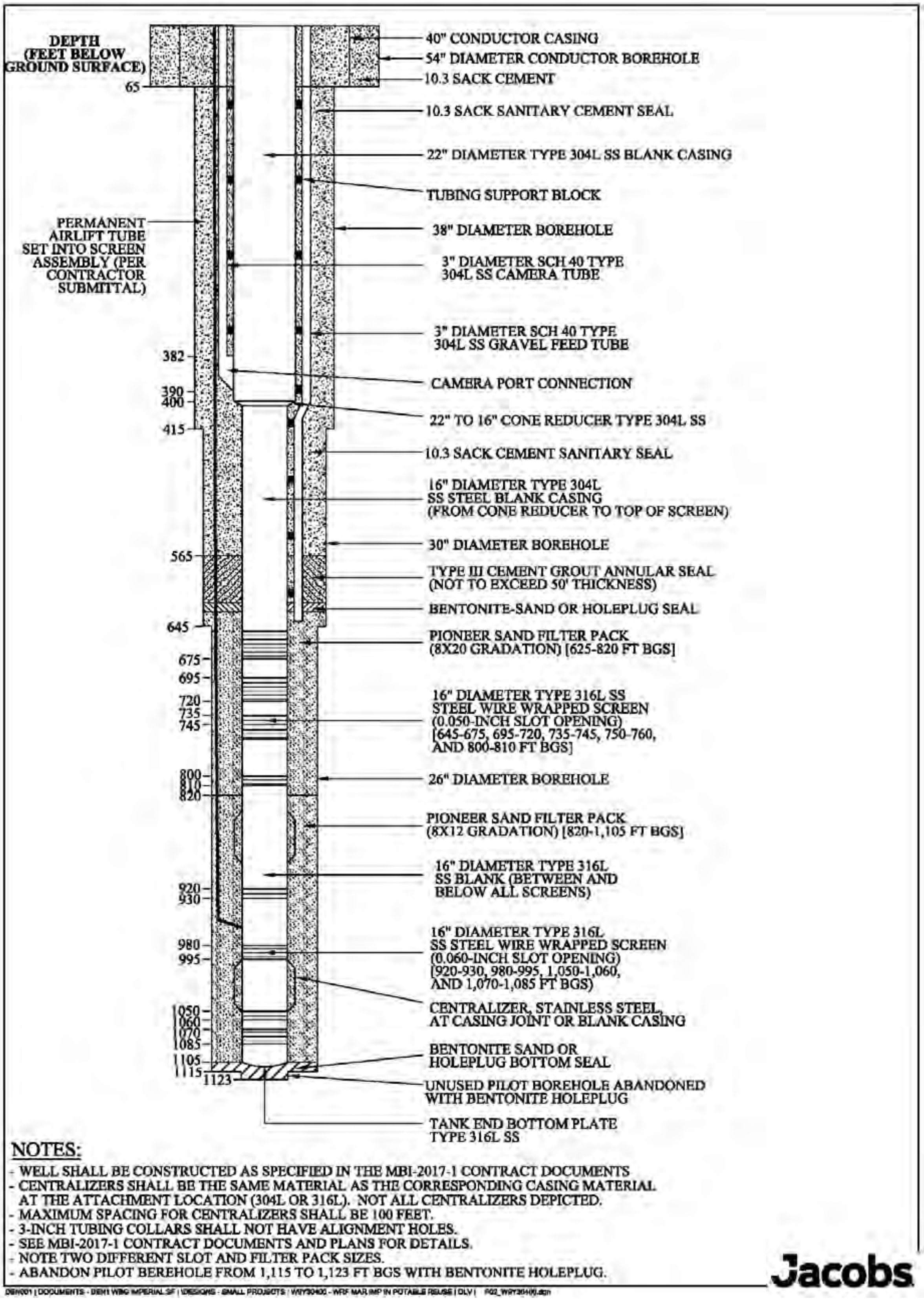
C.1.2 Case Study 1

Despite the reliance on MFI indices to control the frequency of maintenance measures, OCWD successfully runs its MAR operations employing frequent invasive rehab measures (Figure C- 5) routinely to maintain injectivity in their wells. The completed utility survey indicates OCWD maintains over 100 MAR wells ranging in capacity from 10 to 1,500 gpm that recharge up to 50 MGD through the network. More recently, OCWD has established a recharge target of >1 MGD for new MAR wells. Furthermore, OCWD has equipped only eight of the 107 wells with a pump suitable for backflushing, while using airlift pumping via a portable air compressor at the others.

The large number of MAR wells allows OCWD to recharge at lower rates for individual wells while still meeting the AWT demands. Thus, a fraction of the network at any moment may contain several poorly performing wells or wells removed from service awaiting maintenance. OCWD's operating approach may not prove practical for utilities operating MAR facilities in areas devoid of available land for well locations and adequate well spacing. In these systems, every well must operate near peak capacity.

C.1.2.1 Path to a Solution

OCWD employs several distribution maintenance and rehabilitation crews to conduct invasive rehab measures in the form of aggressive mechanical rehab through airlift pumping. In older wells, the crew removes recharge piping and pumps the well through temporarily installed airlift piping. OCWD has equipped newer wells with a dedicated airlift line than extends down the outside of the well casing to a port near the base of the screen assembly (Figure C-10), along with second line installed inside the well to return airlift effluent. Thus, the rehabilitation crew attaches a portable air compressor to the airlift line and conducts airlifting without removing the downhole equipment. OCWD's new configuration allows faster, more efficient and more frequent invasive rehab events, maintaining well injectivity without the capital cost or maintenance of a dedicated backflush pump within each well.



NOTES:

- WELL SHALL BE CONSTRUCTED AS SPECIFIED IN THE MBI-2017-1 CONTRACT DOCUMENTS
- CENTRALIZERS SHALL BE THE SAME MATERIAL AS THE CORRESPONDING CASING MATERIAL AT THE ATTACHMENT LOCATION (304L OR 316L). NOT ALL CENTRALIZERS DEPICTED.
- MAXIMUM SPACING FOR CENTRALIZERS SHALL BE 100 FEET.
- 3-INCH TUBING COLLARS SHALL NOT HAVE ALIGNMENT HOLES.
- SEE MBI-2017-1 CONTRACT DOCUMENTS AND PLANS FOR DETAILS.
- NOTE TWO DIFFERENT SLOT AND FILTER PACK SIZES.
- ABANDON PILOT BEREHOLE FROM 1,115 TO 1,123 FT BGS WITH BENTONITE HOLEPLUG.

Figure C-10. MBI-2 Well Design.

Source: Modified from OCWD 2020.

C.1.3 Case Study 2

The Hampton Roads Sanitation District's (HRSD) Sustainable Water for Tomorrow (SWIFT) Research Facility (SRC) in Suffolk, Virginia recharges a test MAR test well (TW-1) at 1 MGD with water from an AWT relying on flocculation/sedimentation, ozonation, biologically activated carbon, granulated activated carbon, ultraviolet and chlorine disinfection for treatment. HRSD uses SRC to test treatment approaches and MAR well maintenance techniques in anticipation of implementing MAR facilities capable of recharging over 100 MGD throughout its service area.

The level of residential, commercial, and industrial development across HRSD's service area, limits land available for AWT and MAR wells. With limited land availability for MAR wells, HRSD's wells must perform at high levels with limited time for removing wells from service. Recognizing these factors, at SRC, HRSD operators rely heavily on MFI indices in making decisions on the clogging potential of AWT effluent and maintaining the MAR test well as illustrated on Figures C-4 and C-5).

During MAR operations, HRSD gradually increased the frequency of MFI testing from around once per week when starting MAR in May 2018, to approximately daily between April 2019 and July 2020 (Figure C-11). Upon obtaining trends and evaluating anomalies, HRSD has subsequently reduced the testing frequency to three times weekly. MFIs at SRC have averaged up to 28 sec/L^2 per month, with most MFI's during most months falling between 10 and 15 sec/L^2. Still, the MFIs significantly exceed 3 sec/L^2 as recommended in the literature.

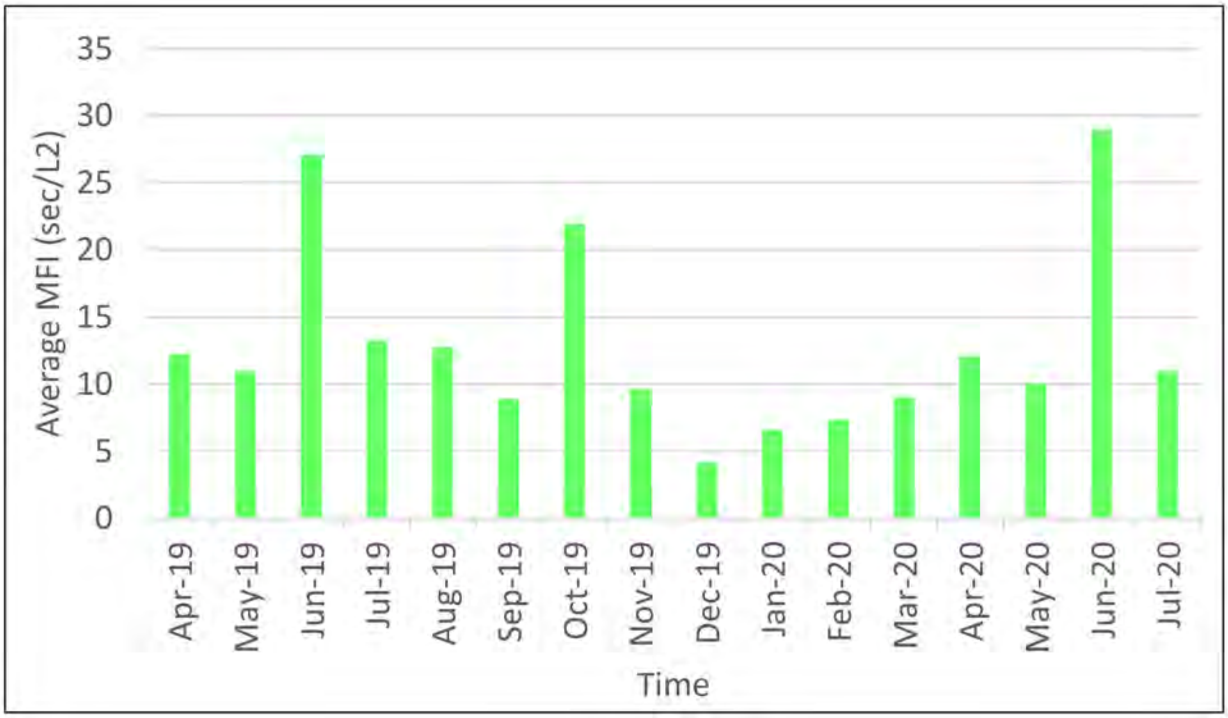


Figure C-11. Average Monthly MFI's – April 2019 to July 2020.

C.1.3.1 Path to a Solution

The injectivity at the SRC test well has reflected the difference between the recommended MFI and operating MFI's with injectivities progressively falling over the period of MAR operations (Figure C-12). As a result, SRC operators have increased the backflushing frequency from three times weekly from May 2018 to November 2018, to daily from April 2019 to December 2019 to every 11 hours from December 2019 to the time of this publication. Backflushing twice daily along with other measures has stabilized injectivities while supporting continuous operation of the facility.

HRSD has continued testing during MAR operations to investigate the origin of injectivity losses. In 2021, HRSD is now evaluating the following:

- Zeta potential of recharge effluent discharged from granulated activated carbon filters.
- Differing injectivities from several GAC filters.
- Wellhead filtration.
- Size of particles entrained in recharge water.
- Chlorine attenuation in aquifer.

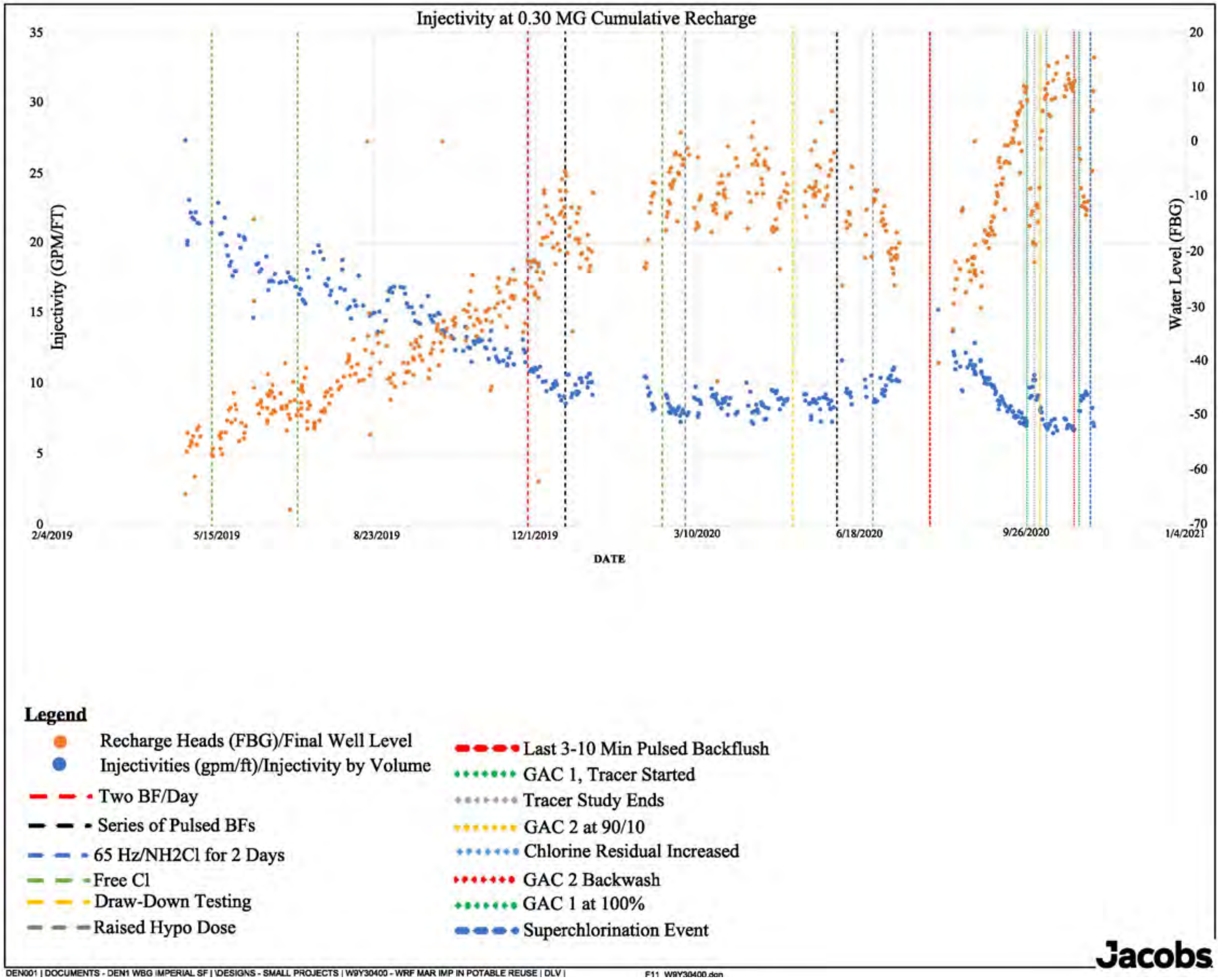
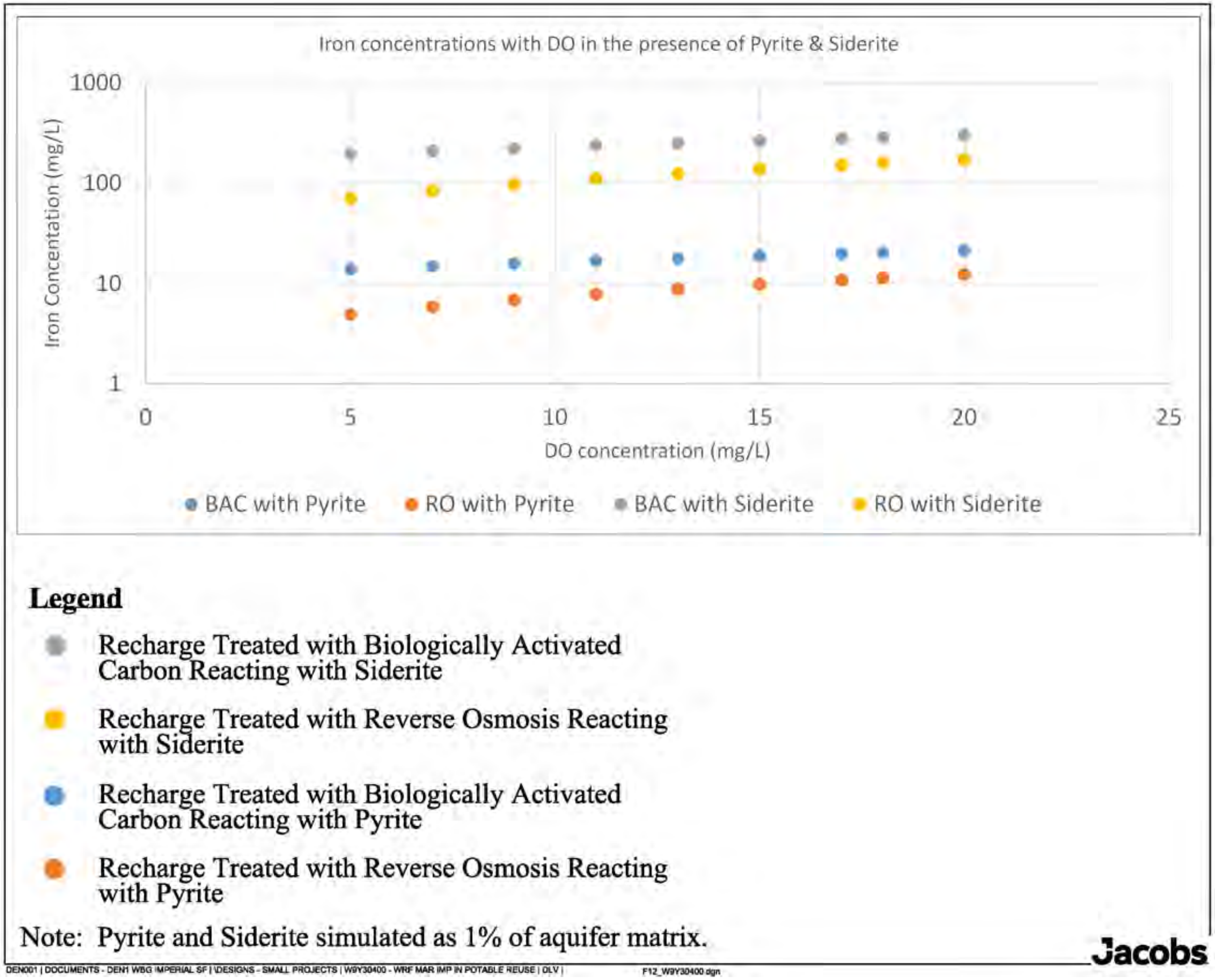


Figure C-12. Injectivity Graph with Specific Events – April 2019 to November 2021.

C.2 Metals Mobilization

Reactions between the recharge water and aquifer matrixes can dissolve minerals, releasing their elemental components to the groundwater (Stuyfzand 1993). Dilute recharge water containing DO injected into an anoxic aquifer will interact with common, reduced metal-bearing minerals like pyrite (FeS_2) and siderite ($FeCO_3$) through reactions including sulfide oxidation, mineral dissolution, pH reduction, competitive desorption, etc. that release iron (Figure C-13) and manganese along with undesirable trace metals that occupy sites in the mineral structure. Oxidation of arsenian pyrite can release arsenic, creating a water quality concern in the migrating recharge. Left unchecked, leaching metals degrade the quality of water stored in the aquifer, violating Safe Drinking Act regulations, while limiting the use of the migrating recharge for potable use.

As the oxidation process continues, iron and manganese released by mineral dissolution are converted to more oxidized forms (Fe (II) to Fe (III); Mn (II) to Mn (III) and Mn (IV)) and reprecipitate as oxide and hydroxide minerals. Increasing the recharge water pH hastens precipitating hydroxide mineral phases, buffering the dissolution of reduced iron-bearing minerals remaining in the matrix. The reaction precipitates HFO on the surface of reactive minerals, isolating the mineral and reducing (passivating) its reactivity in the aquifer. Removing DO from recharge using membranes (CDM 2006), sulfides (Pearce and Waldron 2010), or other techniques precludes the sulfide oxidation reaction, and has worked effectively during testing at ASR facilities. Yet operational success has proven disappointing. Deoxygenation using membranes imposes significant costs on a utility, while employing sulfides produces significant amounts of iron that exceed SMCLs at local monitoring wells.



Note: Pyrite and Siderite simulated as 1% of aquifer matrix.

Figure C-13. Dissolved Iron Concentrations Released by Pyrite and Siderite Reacting with DO Simulated with PHREEQC.

C.2.1 Case Study—Beenyup Groundwater Replenishment Scheme, Water Corporation, Perth, Australia

Samples collected at monitoring wells located up to 150 feet from MAR wells operated by the Water Corporation in Perth Australia, exhibited concentrations of nickel but they did not exceed the Australian Drinking Water Guidelines. However, cobalt exceeded the ADWG of 0.001 mg/L. The survey completed by WC's scientists indicates that WC operates eight MAR wells recharging up to 7.4 MGD daily. WC operates MAR wells in the Cretaceous-Age, Leederville and Jurassic-Age, Yarragadee Aquifers. Cobalt and nickel appeared in groundwater samples collected from a monitoring well(s) screening the Yarragadee Aquifer.

C.2.1.1 Recharge, Groundwater, and Migrating Recharge Chemistries

Entries on the utility survey supported describing the recharge, groundwater and migrating recharge chemistry at the Beenyup Groundwater Replenishment Scheme.

Recharge Water Chemistry

The Water Corporation's AWT treats recharge using membranes, degassing for stabilization, UV and monochloramine for disinfection. The recharge chemistry (Table C-1) reflects the treatment processes in the AWT, producing a dilute, circumneutral (pH 7.2), sodium chloride water (Figure C-14). TDS concentrations fall to less than 25 mg/L (ionic strength 6.0 x 10-4 m/L) with sodium, alkalinity, and chloride representing the main ions, display individual concentrations falling below 10 mg/L. Dissolved oxygen concentrations approach the saturation limit of 8 to 12 mg/L. A computer program developed by the United States Geological Survey (Jurgens, et al. 2009) that evaluates of the common redox indices (Tables C-2 and C-3) including DO, nitrate, manganese, iron, and sulfate returned oxic and oxygen reduction for the main redox category and process, respectively.

Table C-1. Summary of Water Quality at WC Beenyup MAR Facility.

			Groundwater		Migrating Recharge	
Constituent	**Units**	**Recharge**	**Leederville**	**Yarragadee**	**Leederville**	**Yarragadee**
pH	standard units	7.22	7.25	8	7.2	6.8
Dissolved oxygen	mg/L	8	<1	<1	<1	<1
TDD	mg/L	24	510	191	58	47
Calcium	mg/L	0.05[a]	30	10	2	2
Magnesium	mg/L	0.05[a]	13	5	2	1
Sodium	mg/L	8.1	120	54	13	13
Chloride	mg/L	6	250	38	9	8
Sulfate	mg/L	0.05[a]	17	1	12	13
Alkalinity	mg/L	9	59	129	18	4
Iron	mg/L	<0.01	6	0.04	1.5	0.1
Manganese	mg/L	<0.001	0.063	0.006	0.03	0.01
Arsenic	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001

[a] Concentration = 1/2 method detection limit

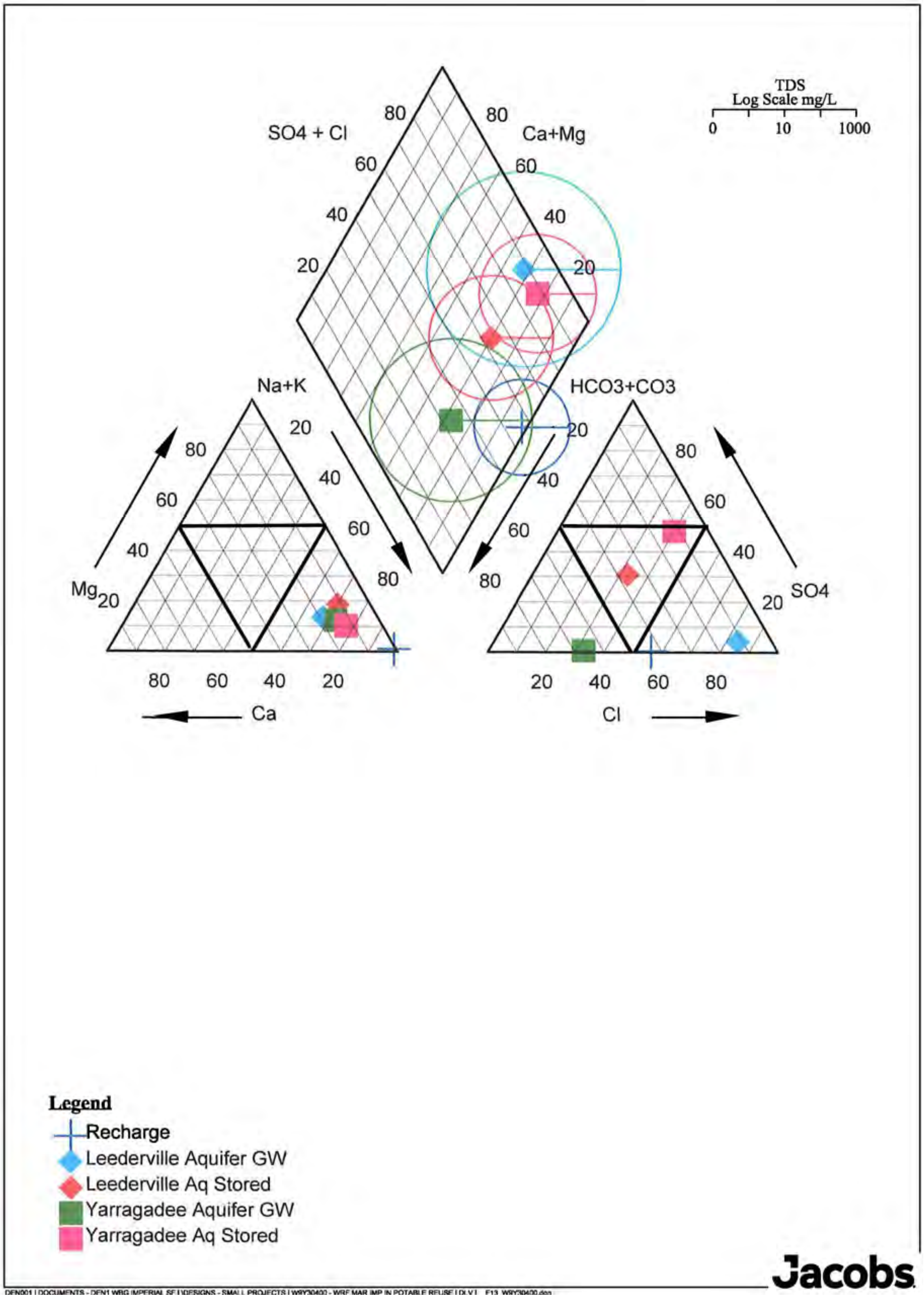


Figure C-14. Piper Diagram of Major Ions in Recharge, Groundwater, and Migrating Recharge at Water Corporation’s Beenyup Groundwater Replenishment Scheme.

Table C-2. Criteria and Threshold Concentrations for Identifying Redox Processes in Ground Water.

Redox category	Redox process [a]	Electron acceptor (reduction) half-reaction[b]	Criteria for inferring process from water-quality data					
			Dissolved oxygen (mg/L)	Nitrate, as Nitrogen (mg/L)	Manganese (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Iron/sulfide (mass ratio)
Oxic	O2	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	≥0.5	—	<0.05	<0.1	—	
Suboxic	Suboxic	Low O2; additional data needed to define redox process	<0.5	<0.5	<0.05	<0.1	—	
Anoxic	NO3	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6\,H_2O$; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	<0.5	≥0.5	<0.05	<0.1	—	
Anoxic	Mn(IV)	$MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	<0.5	<0.5	≥0.05	<0.1	—	
Anoxic	Fe(III)/SO4	Fe(III) and (or) $SO4^{2-}$ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	no data
Anoxic	Fe(III)	$Fe(OH)_{3(s)} + H^+ + e^- \rightarrow Fe^{2+} + H_2O$; $FeOOH_{(s)} + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	>10
Mixed(anoxic)	Fe(III)-SO4	Fe(III) and $SO4^{2-}$ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	≥0.3, ≤10
Anoxic	SO4	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	<0.3
Anoxic	CH4gen	$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$	<0.5	<0.5	—	≥0.1	<0.5	

Table was modified from Jurgens et al. 2009.

[a] Redox Process: O2, oxygen reduction; NO3, nitrate reduction; Mn(IV), manganese reduction; Fe(III), iron reduction; SO4, sulfate reduction; CH4gen, methanogenesis

[b] Chemical species: O2, dissolved oxygen; NO3-, dissolved nitrate; MnO2(s), manganese oxide with manganese in 4+ oxidation state; Fe(OH)3(s), iron hydroxide with iron in 3+ oxidation state; FeOOH(s), iron oxyhydroxide with iron in 3+ oxidation state; SO42–, dissolved sulfate; CO2(g), carbon dioxide gas; CH4(g), methane gas

— criteria do not apply because the species concentration is not affected by the redox process

Table C-3. Summary of Redox Assignments for Samples from WC Beenyup GWRS.

Sample ID	*Redox Variables*[a]	*O_2*	*NO_3^- (as Nitrogen)*	*Mn^{2+}*	*Fe^{2+}*	*SO_4^{2-}*	*Sulfide (sum of H_2S, HS^-, S^{2-})*	*Redox Assignment*			*Fe^{2+}/ Sulfide, ratio*
	Units	(mg/L)	(mg/L)	(µg/L)	(µg/L)	(mg/L)	(mg/L)				
	Threshold values	0.5	0.5	50	100	0.5	none	Num of Params	General Redox Category	Redox Process [2]	
Recharge		10	1.3	0.01	0.0001	0.05	0.01	6	Oxic	O2	
Leederville Aq GW		0.01	0.005	63	4400	17	0.05	6	Anoxic	Fe(III)	
Yarragadee Aq GW		0.01	0.005	6	33	1	0.03	6	Suboxic	Suboxic	
Leederville Aq Migrating Recharge		0.01	0.7	30	1500	12	0.03	6	Mixed(anoxic)	NO3-Fe(III)	
Yarragadee Aq Migrating Recharge		0.01	0.04	12	100	13	0.01	6	Mixed(anoxic)	Fe(III)-SO4	

[a] Redox variables: O2, dissolved oxygen; NO3- (as N), dissolved nitrate; Mn2+, manganese ion; Fe2+, ferrous iron; SO42–,sulfate.

[2] Redox Process: O2, oxygen reduction; NO3, nitrate reduction; Fe(III), iron reduction; SO4, sulfate reduction.

Groundwater Chemistry

The following section describe the groundwater chemistry in the Leederville and Yarragadee Aquifers respectively.

Leederville Aquifer

Groundwater samples from the Leederville Aquifer displayed a fresh water (TDS < 1,000 mg/L) with a circumneutral pH and sodium chloride chemistry. Iron concentrations at around 1.5 mg/L significantly exceeded ADWG of 0.3 mg/L while manganese were below the standard of 0.05 mg/L at 0.03 mg/L. Arsenic concentrations in groundwater from the Leederville Aquifer were below laboratory method detection limits (MDL). Evaluation of redox species produced anoxic and iron-reducing conditions for the redox category and redox process, respectively. The modestly elevated sulfate concentrations suggest that pyrite oxidation may occur in the Leederville Aquifer.

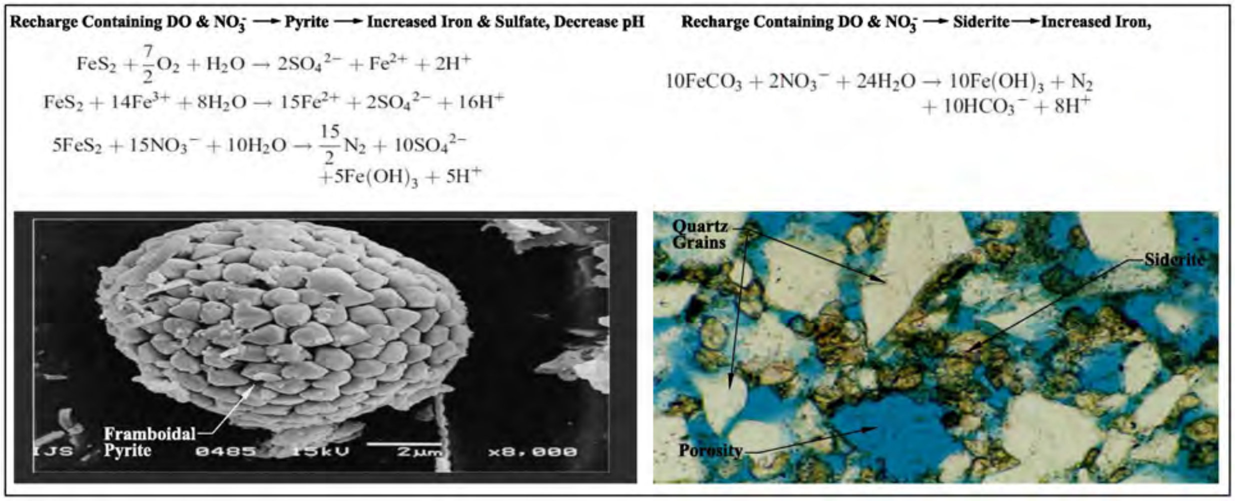
Yarragadee Aquifer

Groundwater from the Yarragadee Aquifer exhibited fresh, mildly alkaline, sodium bicarbonate chemistry. Despite its greater depth, TDS concentrations in the Yarragadee Aquifer were below concentrations in the Leederville Aquifer, suggesting differing sources of recharge and likely minimal vertically downward recharge through Leederville Aquifer. Iron, manganese, and arsenic concentrations fluctuated around their respective MDL's and did not exceed ADWG. Sulfate concentrations equaled around 1 mg/L suggesting pyrite oxidation does not naturally occur in the Yarragadee Aquifer

Migrating Recharge

The quality of migrating recharge samples from both the Leederville and Yarragadee Aquifers suggests migrating recharge had passed the respective monitoring wells prior to collecting the samples containing cobalt and nickel in the Yarragadee Aquifer. Both sets of samples showed chemistry that differed significantly from the groundwater from each aquifer.

Recharge migrating in the Leederville Aquifer displayed evidence of reacting with the aquifer minerals. In comparing the recharge and migrating recharge chemistries, the difference comprised diminished nitrate, with increased concentrations of iron, manganese, sulfate and alkalinity (Figure C-15). The pH of the migrating recharge remained equivalent to recharge prior to entering the Leederville Aquifer. The highly elevated iron, manganese, sulfate and alkalinity infers that recharge reacted with the iron carbonate mineral, siderite (FeCO3) along with pyrite (FeS2), the most common sulfide mineral (Evangelou 1995). Water-rock reactions produced a more buffered migrating recharge that maintained a stable pH, but still elevated sulfate concentrations. Migrating recharge in the Leederville Aquifer displayed a sodium—mixed anion chemistry compared to the sodium chloride chemistry displayed by recharge.



Recharge Containing DO & NO_3^- → Pyrite → Increased Iron & Sulfate, Decrease pH

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow 2SO_4^{2-} + Fe^{2+} + 2H^+$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

$$5FeS_2 + 15NO_3^- + 10H_2O \rightarrow \frac{15}{2}N_2 + 10SO_4^{2-} + 5Fe(OH)_3 + 5H^+$$

Recharge Containing DO & NO_3^- → Siderite → Increased Iron,

$$10FeCO_3 + 2NO_3^- + 24H_2O \rightarrow 10Fe(OH)_3 + N_2 + 10HCO_3^- + 8H^+$$

Figure C-15. Pyrite and Siderite Dissolution during MAR Operations.

In addition to cobalt and nickel, groundwater samples from the Yarragadee Aquifer displayed other prominent geochemical indices including reduced pH, nitrate and alkalinity, plus increased concentrations of iron, manganese, and sulfate. Elevating sulfate concentrations proved sufficient to change the ionic composition from a sodium bicarbonate in the recharge to a sodium-mixed anion-sulfate chemistry in the migrating recharge. Thus, migrating recharge from the Yarragadee Aquifer exhibits evidence of the abiotic oxidation of pyrite (FeS_2). Declining nitrate concentrations suggests, that in addition to DO, nitrate may also serve as an electron acceptor during the oxidation of pyrite.

Arsenic concentrations greater than MDLs did not appear in migrating recharge in samples from the Leederville or Yarragadee Aquifer. Moreover, even though migrating chemistry from both aquifers showed evidence of pyrite oxidation, nickel and cobalt emerged only in samples from the Yarragadee Aquifer, indicating that the pyrite composition between the two units differs.

C.2.1.2 Path to a Solution

The Decision Framework flowcharts for Phase 1 and Phase 2 (Figures C-16 and C-17) identify the potential for treating cationic metals in situ. A flowchart describing processes for stabilizing reactive minerals in situ offers two potential pathways (Figure C-18) toward stabilizing reactive minerals in situ. The first involves removing oxidants, specifically DO from the recharge using membranes, sulfides by chemical addition, or air stripping.

The Water Corporation's survey mentions taking measures to prevent air entrainment by installing a downhole control valve (DHCV) on the recharge line. By constricting the recharge line using a sliding sleeve or packer (Figure C-19) DHCV's control head, by backing water up the column, producing a positive pressure at the wellhead. The measure prevents forming a vacuum in the recharge line and entraining air through the line or connecting wellhead. However, a DHCV cannot remove DO or nitrate already dissolved in the recharge.

The second approach, most applicable to iron-rich environments like the Leederville or Yarragadee Aquifers entails precipitating hydrous ferric oxide (HFO) coatings on the surface of pyrite and/or siderite (Figure C-20). The process involves adjusting the pH above 8 in combination with DO already dissolved in the recharge, or potentially adding gaseous DO . The HFO coating reduces the reactivity (passivation) of the mineral while developing highly adsorptive surfaces that adsorb iron, manganese, nickel, cobalt (Figure C-21), or oxy-anions like arsenic transported in the migrating recharge (Hayakawa, et al. 2013; Dzomback and Morel 1990; Garrels 1960). Increasing the recharge pH hastens the kinetics of precipitation and passivation of reactive minerals.

The low alkalinity of the recharge at 9 mg/L may require adding an agent like gaseous carbon dioxide to increase the buffering capacity of the recharge. Adding a buffering agent will help maintain the pH of the migrating recharge while countering acid production during pyrite oxidation. As mentioned above regarding drawbacks to removing DO from recharge, adding multiple chemical feed systems to stabilize minerals in situ can prove challenging, particularly dialing in the effective dosage of each chemical.

C.2.2 Metals Mobilization—Arsenic

Worldwide, numerous sites operating MAR (potable, reclaimed and stormwater) and ASR facilities have reported issues with encountering concentrations of arsenic elevated above drinking water standards at sentinel monitoring wells or contained in the recovered water from ASR wells. As mentioned previously in Chapter 4, common processes (Fakhreddine et al. 2015) triggering arsenic release into migrating recharge include:

- Competitive desorption by other oxy-anions like phosphate
- Desorption by recharge exhibiting alkaline pH
- Reductive dissolution of metal oxide surfaces hosting adsorbed arsenic
- Oxidative dissolution of arsenic-bearing minerals like arsenian pyrite.

Given the number of arsenic releasing mechanisms, possible recharge and groundwater chemistry combinations, mineral compositions in receiving aquifers and the hazardous nature of arsenic imposed on potential drinking water aquifers, releasing arsenic into migrating recharge represents a major concern for MAR operations.

Phase 1. Geochemical Compatibility Investigation for Managed Aquifer Recharge (MAR) Projects

Phase Objectives

- Identify cheochemical issues that could compromise the project's success
- Identify geochemical challenges and solutions for successful operations
- Describe data gaps that need addressing to:
  1. Develop design criteria
  2. Establish procedures to sustain MAR operations while protecting water quality in receiving aquifer

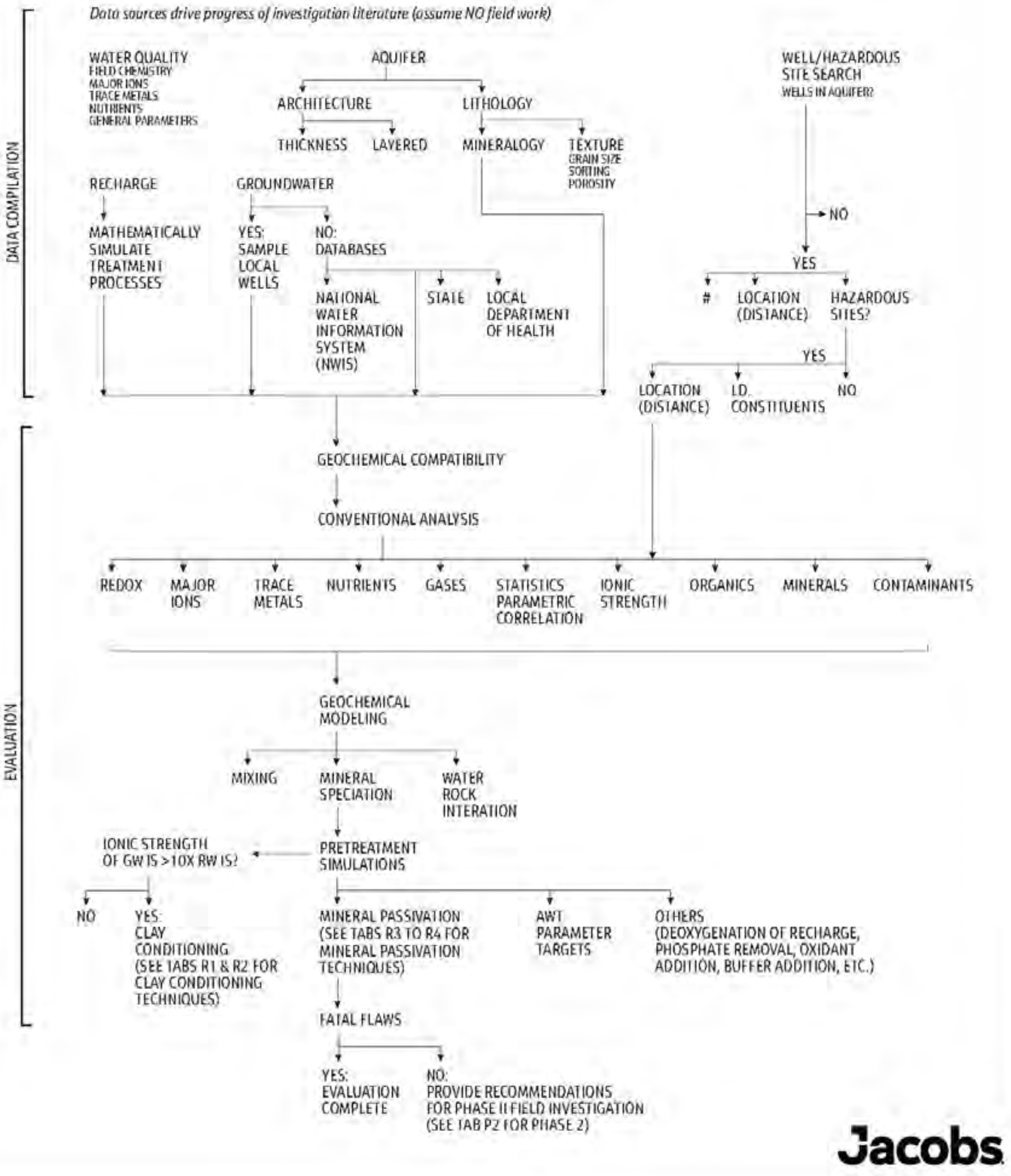


Figure C-16. Decision Framework Flowchart for Phase 1 Analysis.

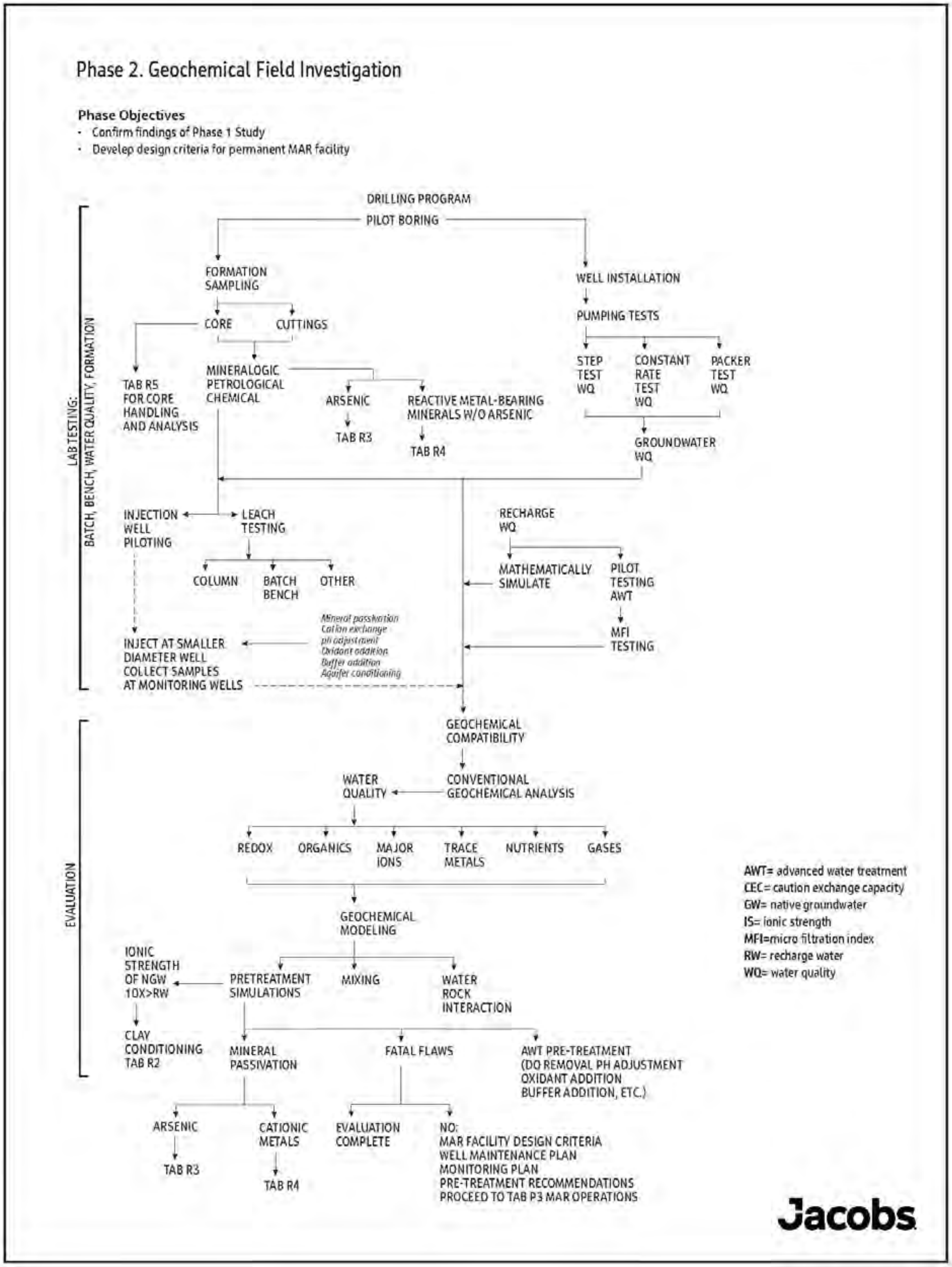


Figure C-17. Decision Framework Flowchart for Phase 2 Field Investigation.

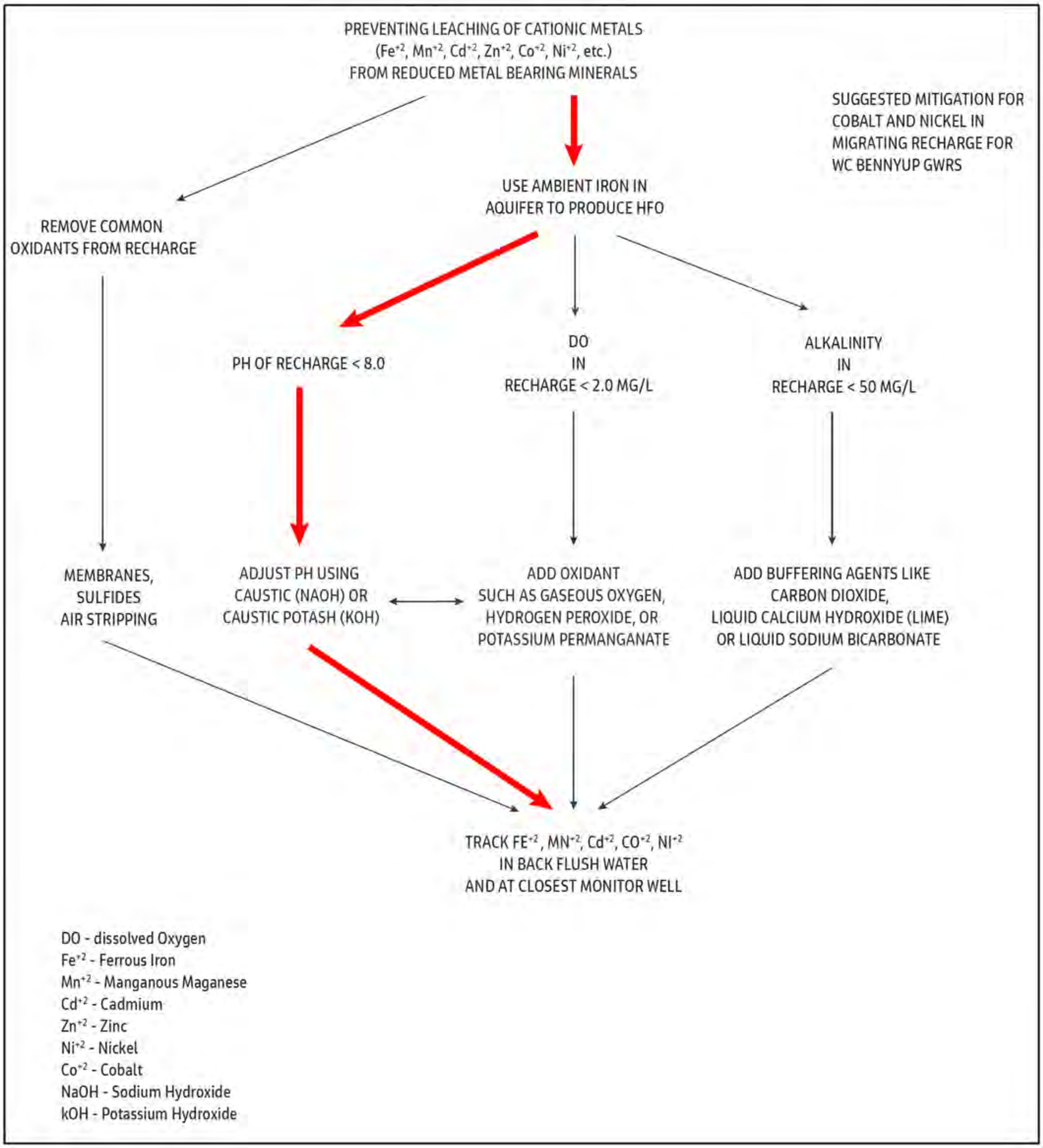


Figure C-18. Decision Framework Flowchart for Mitigating Cationic Metals at Water Corporation's Beenyup Groundwater Replenishment Scheme.

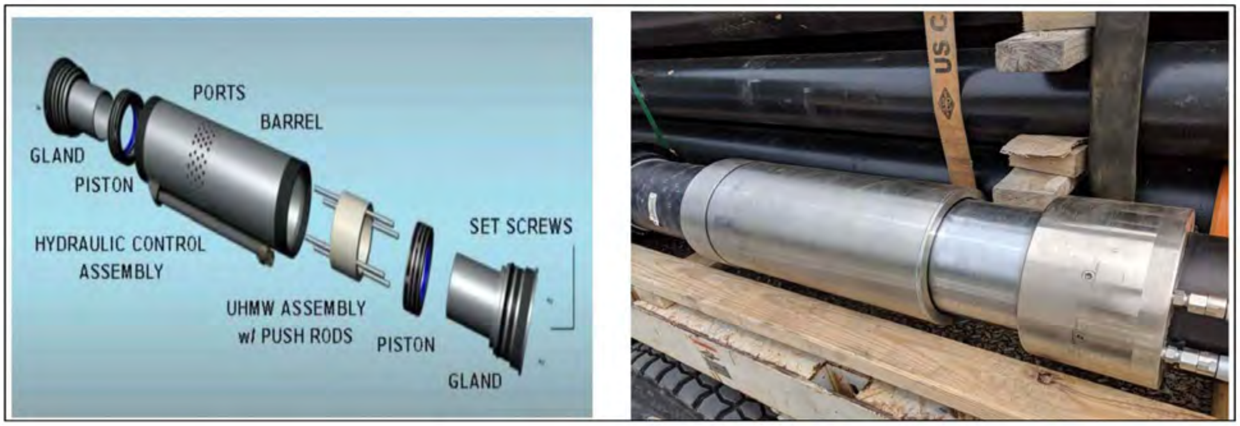


Figure C-19. Examples of Downhole Control Valves.

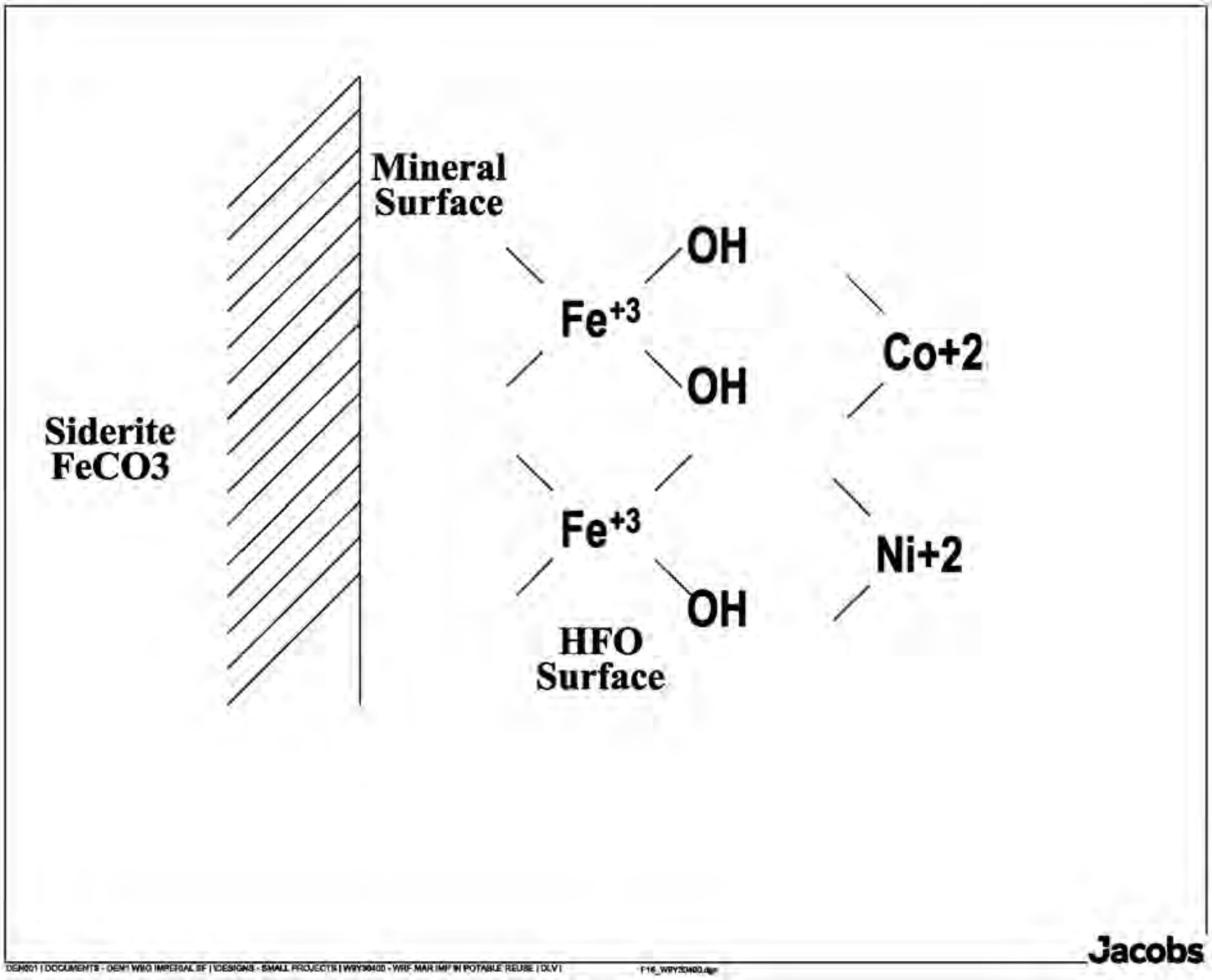


Figure C-20. HFO Surface on Siderite Adsorbing Cobalt and Nickel Ions.

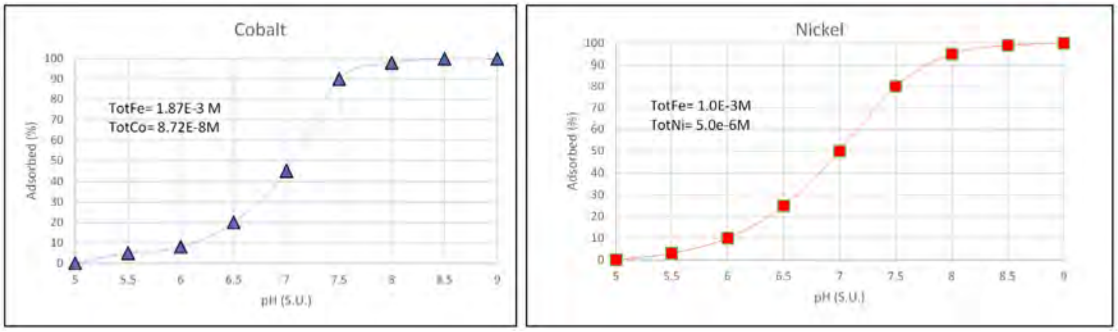


Figure C-21. Adsorption Isotherms for Cobalt and Nickel on HFO.

C.2.2.1 Case Study- OCWD's Groundwater Replenishment System

This case study again focuses on operations at OCWD's Groundwater Replenishment System and originally appeared in a refereed article published in Environmental Science and Technology in 2015 (Fakhreddine, et al. 2015). The case study describes non-redox related arsenic desorption from clay minerals after infiltration of high purity recharge into a surficial aquifer displaying oxic redox conditions.

Arsenic resides in sediments comprising the surficial aquifer underlying infiltration basins of the Orange County Groundwater Basin. This case study examines conditions at mobilization of arsenic from aquifer sediments deposited by the Santa Ana River underlying the Miraloma Basin complex located in Anaheim, California.

Recharge

OCWD's Groundwater Replenishment System project produces high purity recharge involves treating secondary-treated wastewater from the Orange County Sanitation District using microfiltration/ultrafiltration, reverse osmosis, and ultraviolet light with hydrogen peroxide addition for advanced oxidation. Prior to recharge the OCWD, operator of the AWT, stabilizes the recharge to protect distribution system piping using partial decarbonation and quicklime addition. Infiltration of the high purity recharge into the Miraloma Basin has resulted in transient spikes of arsenic at proximal monitoring wells. Arsenic concentrations and the frequency of its appearance diminishes with time distance from the MAR basins. Prior to infiltration, Groundwater Replenishment System recharge water does not contain detectable arsenic above the standard drinking water analytical method reporting limit of 1 µg/L. Native or antecedent groundwater in the Forebay area prior to the introduction of Groundwater Replenishment System recharge contained arsenic concentrations ranging from non-detect to 6 µg/L, varying spatially and with depth

Recharge chemistry typifies water treated with membranes and thus, exemplifies a likely chemistry that numerous MAR facilities will produce as the number of systems increase. The Groundwater Replenishment System recharge consists of dilute TDS concentrations, running less than 50 mg/L (Table C-4), a slightly alkaline pH (7.8) and mixed cation-bicarbonate (Figure C-22). Containing elevated concentrations of DO and nitrate (1.22 mg/L), recharge display an oxic redox with oxygen reduction representing the primary redox process.

Groundwater

Groundwater in the surficial aquifer displayed TDS (644 mg/L) in the fresh range with concentrations slightly greater than the SMCL of 500 mg/L, with an alkaline pH around 8 and a mixed cation—bicarbonate chemistry, resembling the recharge. TOC concentrations ranged between 1 and 2 mg/L, relatively typical concentrations in groundwater. Redox properties for the groundwater match the recharge, and oxic environment with oxygen reduction representing the primary redox process (Table C-5).

Table C-4. Summary of Water Quality at OCWD MAR Facility.

Constituent	Units	Recharge	Groundwater	Migrating Recharge
pH	standard units	7.8	7.9	
Total organic carbon	mg/L	0.14	5.43	
Calcium	mg/L	8.1	80	
Magnesium	mg/L	<0.1	23	
Sodium	mg/L	8.1	100	
Chloride	mg/L	6.7	126	
Sulfate	mg/L	0.5	141	
Bicarbonate	mg/L	25.6	207	
Nitrate	mg/L	1.22	4.3	

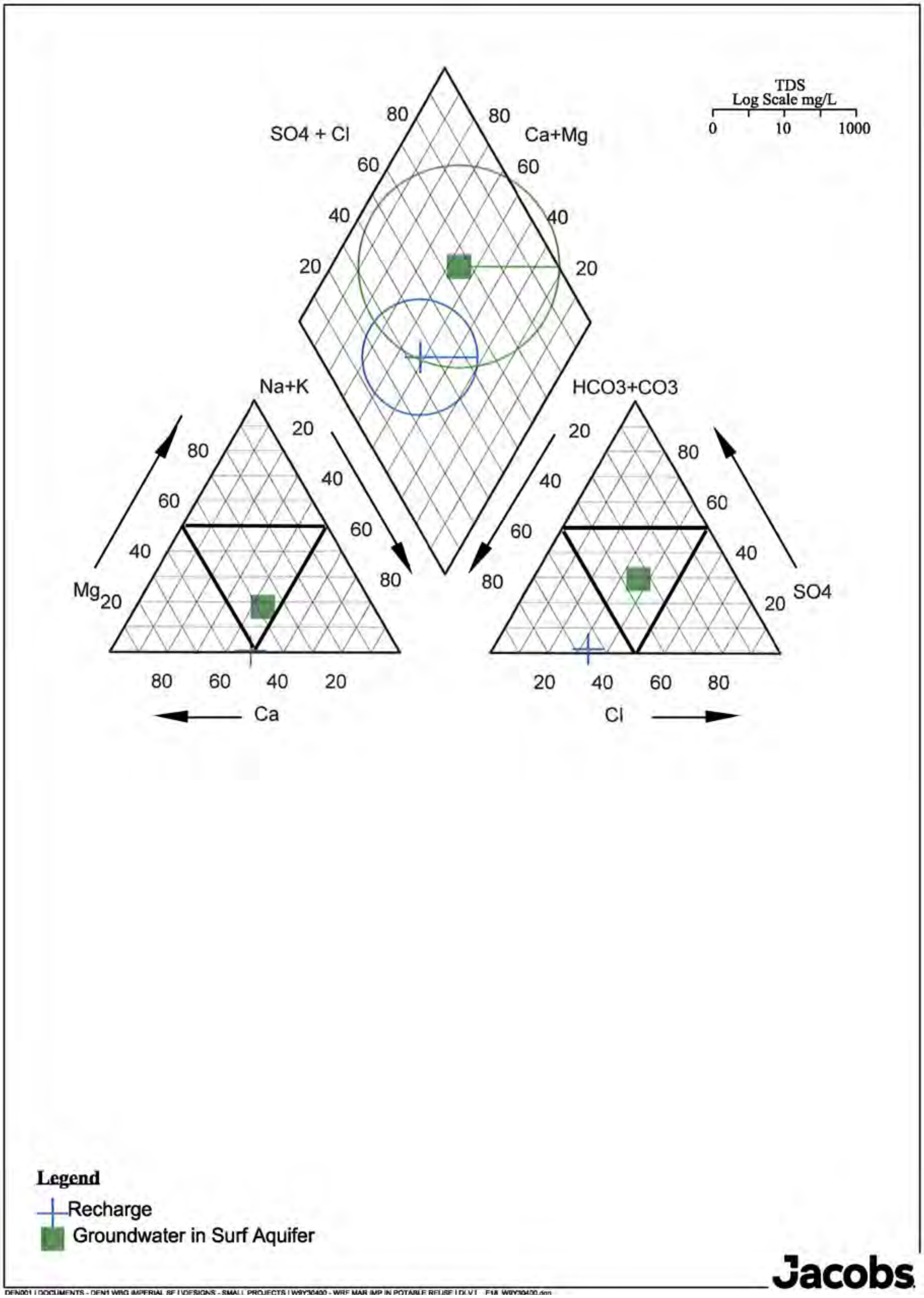


Figure C-22. Piper Diagram of Major Ions in Recharge and Groundwater for Orange County Water District's Groundwater Replenishment System.

Table C-5. Summary of Redox Assignments for Samples from OCWD Groundwater Replenishment System.

	Redox Variables[a]	***O_2***	***NO_3^- (as Nitrogen)***	***Mn^{2+}***	***Fe^{2+}***	***SO_4^{2-}***	***Sulfide (sum of H_2S, HS^-, S^{2-})***	***Redox Assignment***			***Fe^{2+}/ Sulfide, ratio***
	Units	**(mg/L)**	**(mg/L)**	**(µg/L)**	**(µg/L)**	**(mg/L)**	**(mg/L)**				
Sample ID	**Threshold values**	**0.5**	**0.5**	**50**	**100**	**0.5**	**none**	**Num of Params**	**General Redox Category**	**Redox Process** [b]	
OCWD Recharge		6	0.7	1	5	0.5	0.06	6	Oxic	O2	
OCWD Talbert GW		0.3	0.01	19	208	0.3	0.05	6	Anoxic	CH4gen	
OCWD MBI GW		0.04	0.05	9	16	36	0.03	6	Suboxic	Suboxic	
OCWD Forebay GW		0.03	0.01	10	15	0.05	0.03	6	Suboxic	Suboxic	
OCWD Talbert MR		3	1.4	2	2	2.8	0.01	6	Oxic	O2	
OCWD MBI MR		3.2	1	1	6	3.9	0.005	6	Oxic	O2	
OCWD Forebay MR		7	1	3	115	1.2	0.01	6	Mixed (oxic-anoxic)	O2-Fe(III)	11.50

[a] Redox variables: O2, dissolved oxygen; NO3- (as N), dissolved nitrate; Mn2+, manganese ion; Fe2+, ferrous iron; SO42–,sulfate.

[b] Redox Process: O2, oxygen reduction; Fe(III), iron reduction; CH4gen, methanogenesis.

Aquifer Sediments

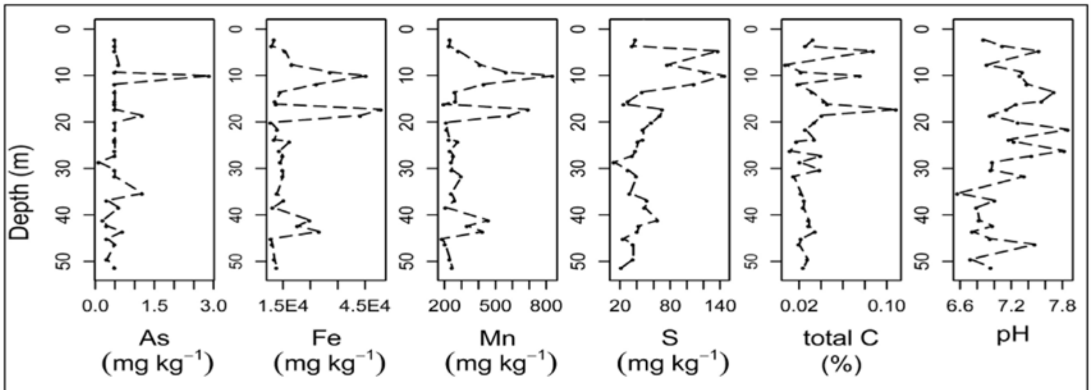
OCWD installed a test well featuring a screened interval extending from 138 to 148 fbg with the water table encountered at 60 fbg. Field personnel collected cores at roughly 2-foot intervals and submitted samples for the following laboratory analysis including:

- Bulk carbon and nitrogen analysis
- X-ray fluorescence (XRF) for bulk arsenic, manganese, iron and sulfide
- X-ray adsorption near-edge spectroscopy (XANES) to determine the oxidation state of arsenic
- Sediment pH
- X-ray diffraction for clay mineral identification

Analysis of the aquifer sediments enabled OCWD to profile the abundance of elemental compositions and pH with depth (Figure C-23). The maximum arsenic concentration measured 2.9 mg/kg, relatively low concentration (Smedley and Kinniburgh 2002) considering the global average for arsenic contained in sediments ranges from 3 to 10 mg/kg. The highest arsenic concentrations correlated with finer-grained horizons. These intervals also displayed the most elevated concentrations of other redox-sensitive elements including iron, manganese, and sulfide. Additionally, slightly greater carbon concentrations correlated with elevated arsenic. Sediment pH fluctuated around neutral and showed negligible correlation with constituent concentrations.

XRD analysis results revealed the clay fraction consisted mostly of vermiculite with small amounts of kaolinite. Arsenic appeared only in the clayey sediments, falling below MDL’s for XRF analyses in coarser-grained sediments. In samples analyzed by XANES, arsenic appeared predominantly as arsenate (As V). Aquifer sediments displayed relatively low carbon concentrations. Moreover, arsenic concentrations in sediments displayed a low correlation coefficient with bulk carbon.

The analyses culminated in a program of laboratory studies including unbuffered batch reactors, buffered batch reactors, and column experiments.



Source: Fakhreddine, et. al., 2015

Figure C-23. Composition of Aquifer Sediments in Test Boring for Orange County Water District's Groundwater Replenishment System.

Study Results

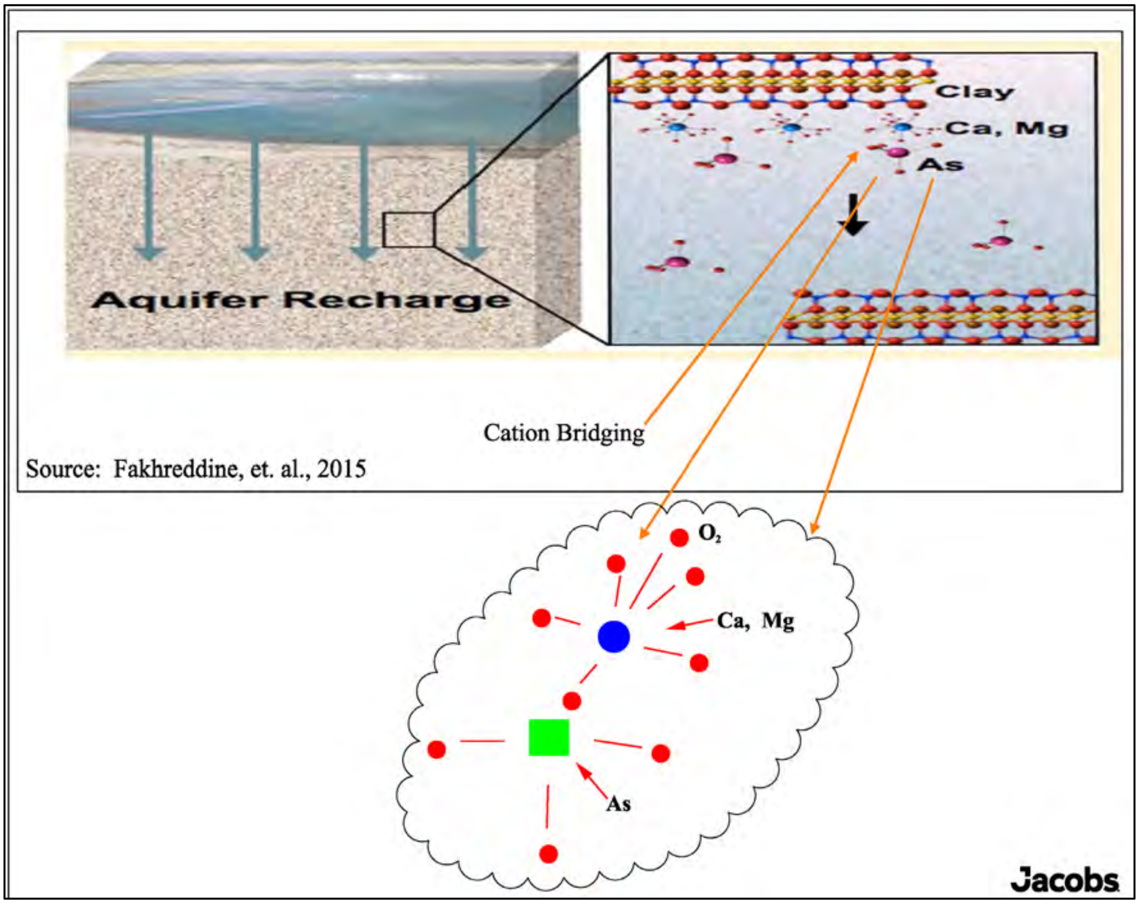
Given the absence of arsenic in the Groundwater Replenishment System recharge water, aquifer solids controlled the release of arsenic into migrating recharge, producing concentration spikes in samples collected from proximal monitoring wells. The suite of solid phase analyses showed arsenic most associated with clayey sediments, with arsenic concentrations correlating with increasing clay content. The low affinity of coarser-grained sediments for arsenic looked consistent with the greater electrostatic -interactions characteristic of clay minerals like vermiculite and smectite (Manning and Goldberg 1997).

Arsenic desorption from clay minerals such as vermiculite can occur as with changes in pH, anion (ligand) exchange and changes in the ionic strength of migrating recharge compared to groundwater. The high purity recharge contained relatively low concentrations of ligands that might compete with arsenic for sites on clay surfaces. Instead, researchers indicated that mechanisms most responsible for arsenic desorption included pH shifts and ionic composition (Smith, et al. 2002). Of the two mechanisms ionic composition appeared more likely to control arsenic release.

Laboratory experiments determined that increasing concentrations of calcium (Ca^{+2}) and magnesium (Mg^{+2}) decreased the amount of arsenic released into the surrounding pore water. The presence of divalent cations appeared most influential while amendments containing Ca^{+2} and Mg^{+2} like dolomitic lime, quicklime, and gypsum decreased arsenic concentrations while improving the effluent from columns.

Calcium and Mg^{+2} can promote arsenic adsorption to permanently charged phyllosilicate surfaces by increasing the positive surface charge and subsequent adsorption of arsenate species ($H_2AsO_4^{-1}$ and $HAsO_4^{-2}$; Smith, et al. 2002). Owing to the constrained effects of ionic strength, a potential mechanism for arsenic retention with Ca^{+2} and Mg^{+2} likely entails cation bridging between negatively charged clay surfaces and similarly charged arsenate ions (Figure

C-24). Other studies have described similar bridging mechanisms involving NaCl but involved a saline environment (Wainpee et al. 2013).



Source: Fakhreddine, et. al., 2015

Figure C-24. Diagram Showing Cation Bridging Between Clays and Arsenic.

Path to a Solution

The flowchart (Figure C-25) describing arsenic mobilization shows the mechanisms and mitigation measures described in this case study, mechanisms not traditionally triggering arsenic release. Unlike most other mechanisms that deal with redox shifts, competitive desorption, or contributing minerals, the situation defined by the case study involves a dilute recharge infiltrating an aquifer containing groundwater of higher ionic strength yet not high enough to prompt treatment with Al-salts. However, adding Ca^{+2} and/or Mg^{+2} can prove expensive to a utility and require appropriately constructed and sized storage facilities along with chemical costs, unless otherwise required for post-treatment stabilization to protect distribution infrastructure.

C.3 Clay Dispersion

Recharge exhibiting a significantly lower ionic strength (fresher) than groundwater reduces the mineral surface charge environment in the aquifer matrix, potentially damaging interstitial clay minerals attached to aquifer framework particles (formation damage), weakening inter-particle attachments, and even diminishing adhesive charges between individual clay layers (Figure

C- 26). Formation damage also arises when recharge contains differing cations than those residing in the exchange positions of clay minerals (Langmuir 1997).

Exchanging cations can disrupt a clay mineral's atomic structure particularly when their atomic radius exceeds the radius of the replaced cation. During exchange, larger cations fragment the tabular structure of clays, shearing off the edges of the mineral.

All these factors cause clay mineral fragments to migrate through the pore spaces of the aquifer. The fragments may eventually block pore throats, reducing the permeability of the aquifer around a MAR well, diminishing the well's injection capacity. Clay minerals accumulating (brush piling) in pore throats (Figure C-27) has proven difficult to reverse through conventional well rehabilitation measures.

Both reactions damage clays, releasing fragments that accumulate in the interstices of sands, rapidly reducing the permeability of the aquifer (formation damage). Reactions in the sensitive areas immediately around the wellbore, where surface areas are small, promotes extensive formation damage through clogging. Surface area increases geometrically away from a MAR well. Therefore, clogging of an individual pore throat at several feet away from the MAR well exerts minimal change on the bulk permeability of the aquifer.

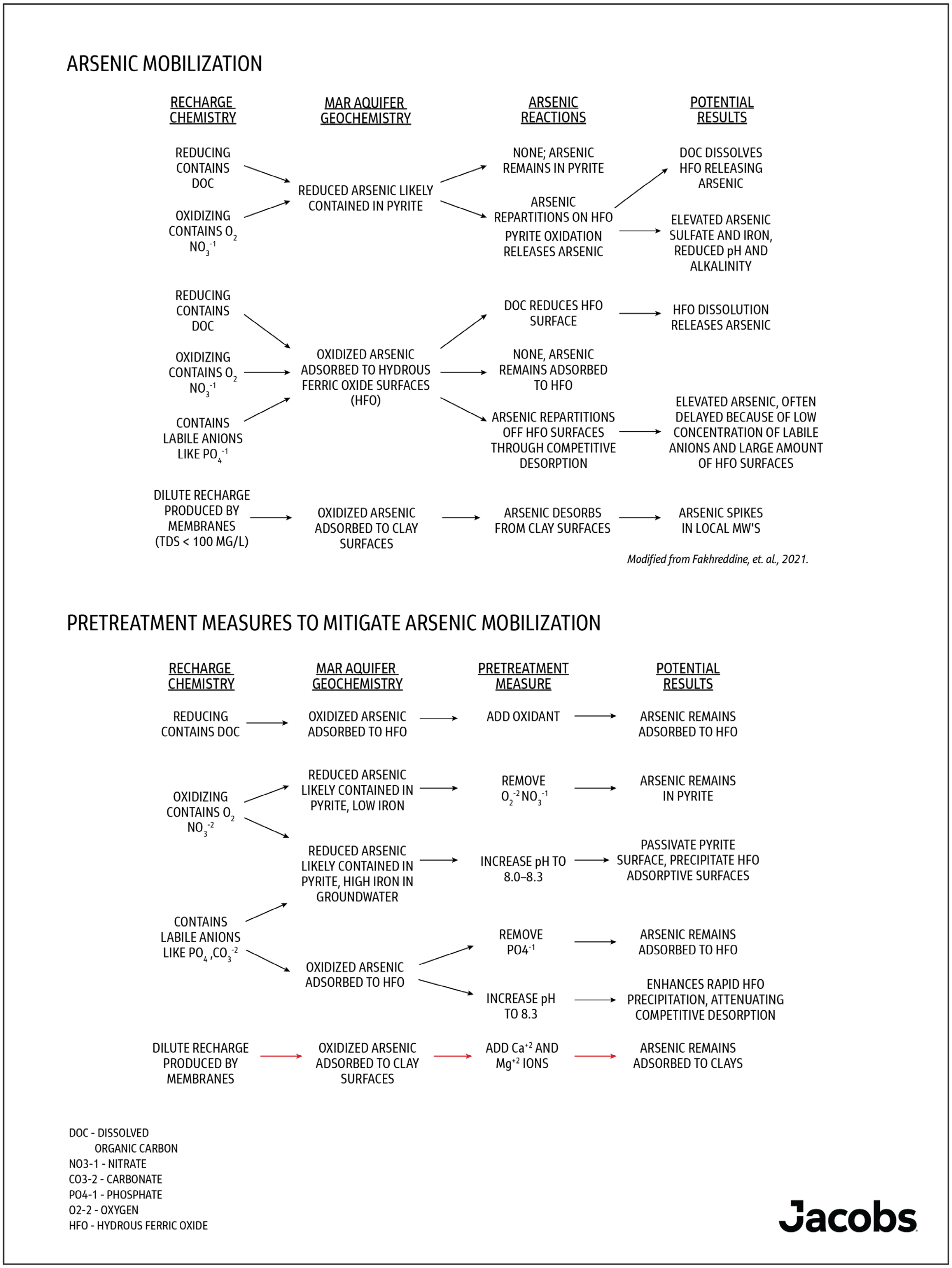


Figure C-25. Decision Framework Flowchart Showing Arsenic Mitigation.

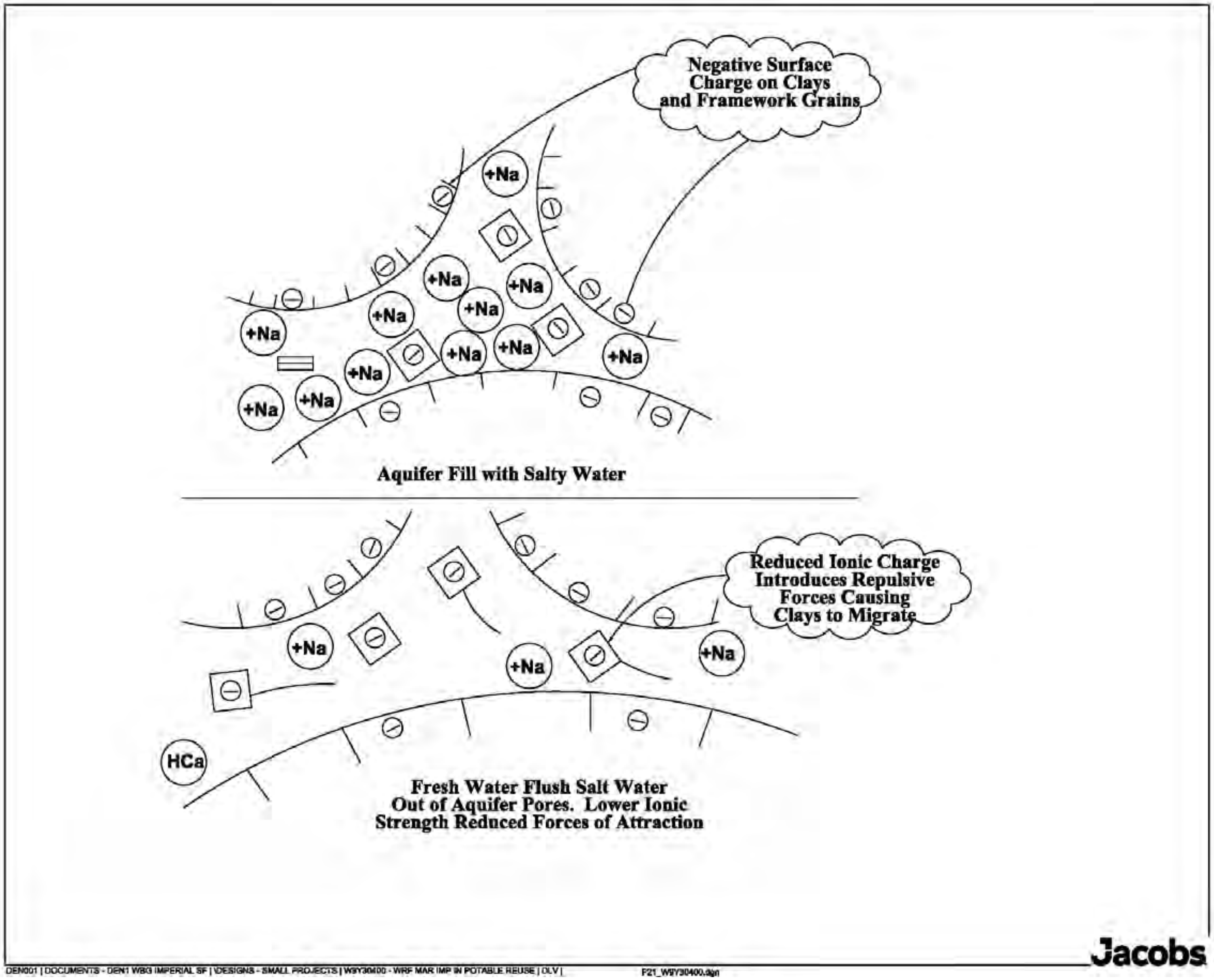
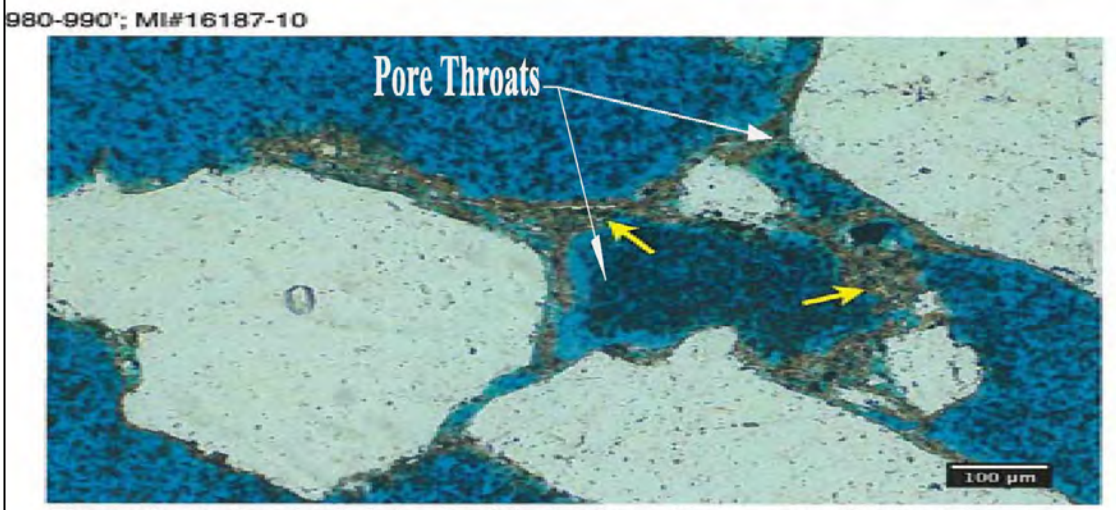


Figure C-26. Effects of Changing Ionic Strength of Native Groundwater.



The grain-coating detrital clay (red) is dominated by montmorillonite. The grain-coating matrix locally bridges the intergranular pore throats (yellow).

Figure C-27. Thin Section Showing Clay Minerals Brush Piling in Pore Throat.

Moreover, the velocity of recharged water progressively declines with distances from a MAR well. Although the cationic chemistry or ionic strength of a recharge water may weaken or expand a clay's mineral structure, the groundwater velocity needs to exceed the shear strength of the damaged mineral to mobilize mineral fragments, and deposit them in a pore throat, to incur formation damage. Subsequently, hydraulic mechanisms that lead to clogging are diminished at distances from the MAR wellbore, while the effects of clogging are widely dispersed and may not influence the bulk permeability of the aquifer.

Medium to fine sand and sandstone aquifers display the greatest vulnerability to clogging by migrating clays. Limestone and extrusive igneous rock aquifers dominated by large pore spaces in lithified rocks rarely suffer problems related to clay dispersion. Further, clay dispersion may show minimal effects in clastic aquifers composed of coarser, well-sorted sands or gravels thus, exhibiting larger and better-connected pore networks. As an example, MAR wells in OCWD's seawater barrier systems, installed in the 1960s and 1970s where the wells recharge fresh water into brackish aquifers have not shown conclusive evidence of formation damage from clay dispersion.

C.3.1 Regional Anecdotal Example

An ASR facility tested by USGS in the 1970s at Norfolk, Virginia exhibited greater than 80 percent reduction in injectivity after only 150 minutes of starting injection operations (Brown and Silvey 1977). The ASR well was installed in the Upper Potomac Aquifer (UPA), screening nearly 85 feet of sand. Groundwater from the UPA displayed a TDS concentration around 3,000 mg/L (ionic strength = 0.08 m/L), while recharge provided by the City of Norfolk exhibited concentrations around 100 mg/L (ionic strength = 0.003 m/L). The USGS employed nuclear, electrical, and mechanical geophysical logging techniques to evaluate the origin of the injectivity losses and discriminate between the causes of clogging documented at other sites, like TSS loading.

Injectivity losses caused by clogging from TSS loading typically occur at discrete zones within the well screen (Jeong, et al. 2018). In contrast, geophysical logging of the ASR test well at Norfolk showed hydraulic conductivity losses distributed evenly across the entire screen. Also, in comparison to clogging by TSS, which responds positively to mechanical and chemical rehabilitations, the USGS could restore only a fraction of the well's original injectivity during invasive rehabilitation.

To arrest the declining injectivity, the USGS treated the wellbore and proximal aquifer with a concentrated calcium chloride ($CaCl_2$>1,000 mg/L) solution. As described above, the doubly charged, calcium cation forms a stronger particle and interlayer bond than the monovalent cation, sodium. Using a concentrated solution ensures calcium exchanges for sodium at the maximum number of sites. After applying the treatment at Norfolk, the injectivity of the ASR test well remained stable (yet low) over two more test cycles, before the project was ended.

C.3.2 Case Study

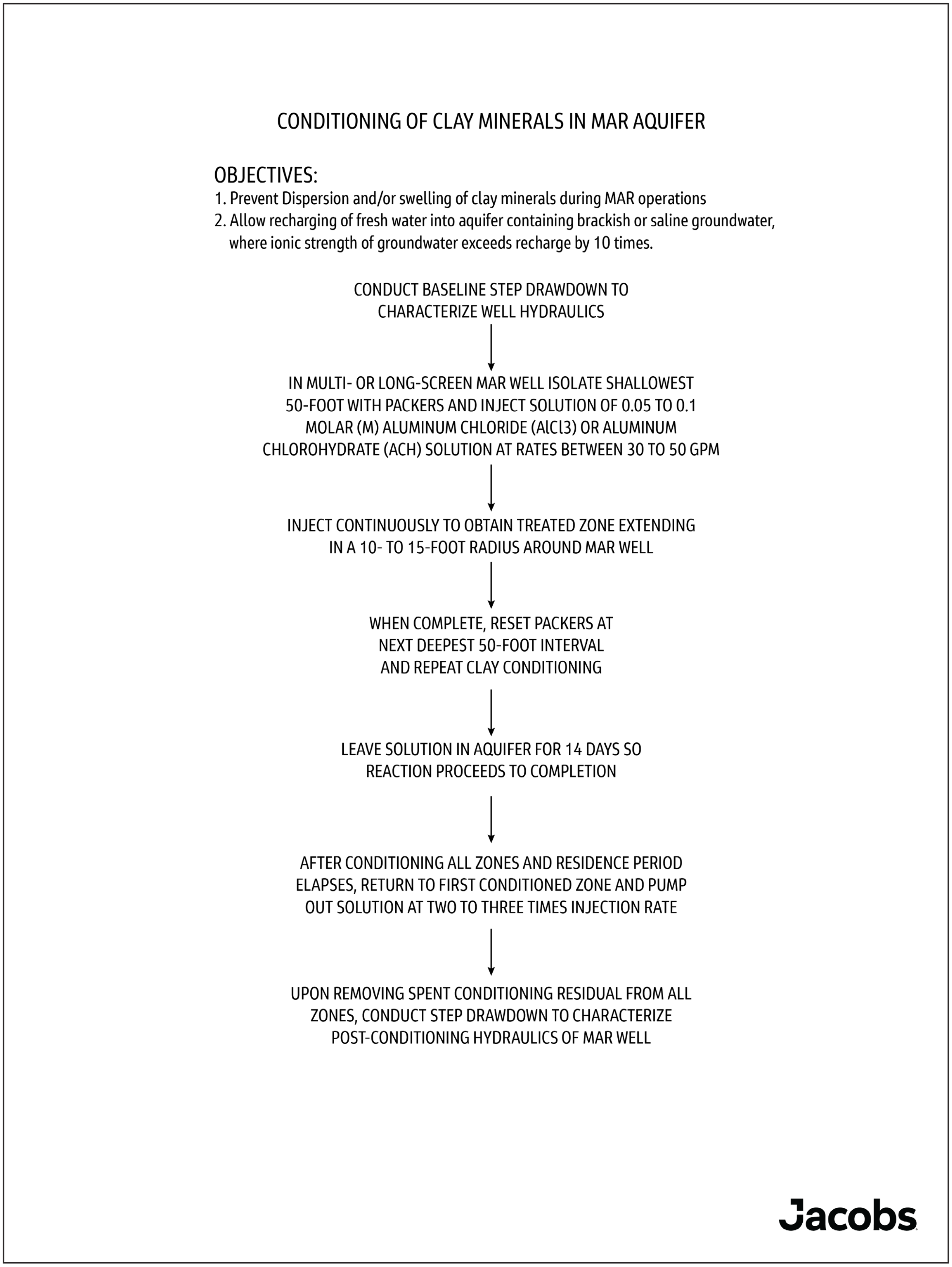
Among the utilities responding to the project's survey, HRSD's SWIFT program represented the only utility now injecting, or planning to inject fresh recharge from an AWT into an aquifer containing brackish groundwater (Table C-6). HRSD's five SWIFT test sites lie adjacent to the coastline of the Atlantic Ocean or the saline James and York Rivers. At the test well TW-5 a facility under consideration, located at HRSD's Virginia Initiative Plant (VIP), the ionic strength of the recharge (0.02 m/L) were nearly two orders of magnitude below the ionic strength of groundwater (0.8 m/L). Thus, clay minerals surrounding the wellbore of TW-5 required conditioning prior to starting MAR operations.

Decision Framework flowcharts describing Phases 1 and 2 of a MAR project describe criteria for initiating aquifer conditioning to prevent clay dispersion (Figures C-16 and C-17), while a subsidiary chart describes the clay conditioning process (Figure C-28) in a step-like manner. Typically, a utility has sufficient information to make the decision to condition clay minerals after Phase 1 and implements conditioning as a field activity during Phase 2 or while constructing the MAR facility during Phase 3.

In aquifers thicker than 50 feet or multi-layer aquifers, employing straddle packers to administer the conditioning improves dispersion through the zones requiring treatment. TW-5 at VIP_SWIFT contained 14 screens ranging in length from 16 to 80 feet (Figure C-29), spanning the entire PAS, including the upper, middle and lower aquifer zones (UPA, MPA, and LPA). Groundwater from the three zones exceeded the ionic strength of the estimated recharge at SWIFT VIP by one order of magnitude or greater. Consequently, recharging fresh water into the PAS, without conditioning would likely result in dispersing clay minerals that occupy interstitial spaces in aquifer sands, clogging aquifer pore throats and reducing the intrinsic permeability of the aquifers. Accordingly, HRSD conditioned the three aquifer zones using a 0.1 M solution of aluminum chlorohydrate (ACH) mixed with potable water from August through December 2019. HRSD conducted the conditioning process in roughly same sequence as displayed on the Decision Framework flowchart.

Table C-6. Summary of Ionic Strengths for MAR Utilities.

	Recharge	Groundwater
Utility	**Ionic Strength (moles/Liter)**	**Ionic Strength (moles/Liter)**
Water Corporation, Beenyup GWRS	6.3E-04	4.8E-5 to 6.1E-2
Water Corporation, Goodman's Point	6.3E-04	4E-2 to 6.5E-2
Tri-Valley Agencies	1.5E-02	1.30E-02
Hampton Roads Sanitation District	1.7E-02	1.40E-02
Anne Arundel County, Maryland	5.8E-03	4E-2 to 9E-4
Valley Water	2.50E-03	5.1E-3 to 1.6E-2
Orange County Water District	1.20E-03	9.0E-03
Truckee Meadows Water Authority	2.50E-03	5.0E-03
Tucson Water	1.20E-02	1.0E-02



CONDITIONING OF CLAY MINERALS IN MAR AQUIFER

OBJECTIVES:

1. Prevent Dispersion and/or swelling of clay minerals during MAR operations
2. Allow recharging of fresh water into aquifer containing brackish or saline groundwater, where ionic strength of groundwater exceeds recharge by 10 times.

CONDUCT BASELINE STEP DRAWDOWN TO CHARACTERIZE WELL HYDRAULICS

↓

IN MULTI- OR LONG-SCREEN MAR WELL ISOLATE SHALLOWEST 50-FOOT WITH PACKERS AND INJECT SOLUTION OF 0.05 TO 0.1 MOLAR (M) ALUMINUM CHLORIDE ($AlCl_3$) OR ALUMINUM CHLOROHYDRATE (ACH) SOLUTION AT RATES BETWEEN 30 TO 50 GPM

↓

INJECT CONTINUOUSLY TO OBTAIN TREATED ZONE EXTENDING IN A 10- TO 15-FOOT RADIUS AROUND MAR WELL

↓

WHEN COMPLETE, RESET PACKERS AT NEXT DEEPEST 50-FOOT INTERVAL AND REPEAT CLAY CONDITIONING

↓

LEAVE SOLUTION IN AQUIFER FOR 14 DAYS SO REACTION PROCEEDS TO COMPLETION

↓

AFTER CONDITIONING ALL ZONES AND RESIDENCE PERIOD ELAPSES, RETURN TO FIRST CONDITIONED ZONE AND PUMP OUT SOLUTION AT TWO TO THREE TIMES INJECTION RATE

↓

UPON REMOVING SPENT CONDITIONING RESIDUAL FROM ALL ZONES, CONDUCT STEP DRAWDOWN TO CHARACTERIZE POST-CONDITIONING HYDRAULICS OF MAR WELL

Figure C-28. Clay Conditioning.

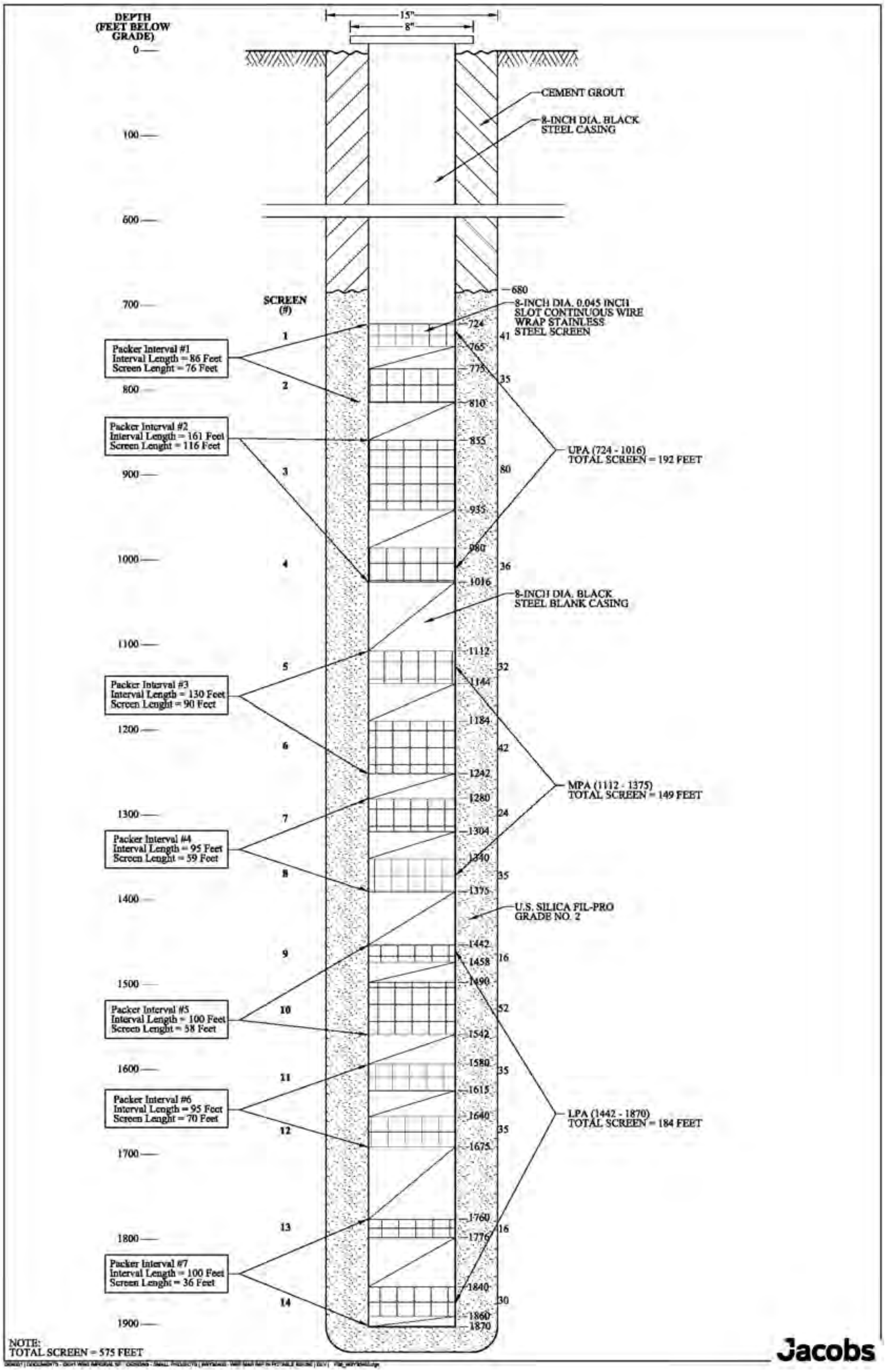


Figure C-29. Construction Detail for HRSD Test Well TW-5 at VIP-SWIFT with Packer Settings for Conditioning.

C.3.2.1 Aluminum Chlorohydrate (ACH)

HRSD conducted extensive studies to identify the agent featuring the best clay stabilization properties. Initial studies revealed that aluminum salt (Al-salt) solutions provided a +3 to +6 charge to form strong charges between the negative surface charge of clay particles and interlayers within clay minerals (Figure C-30). Moving forward, HRSD tested three conditioning solutions comprising aluminum chloride (ALCl3), ACH, and hydroxy-AlCl3, a solution comprising sodium hydroxide and AlCl3 mixed at the site prior to conditioning.

Although strongly advocated by the petroleum industry in preparing reservoirs for water flooding, hydroxy-AlCl3 proved difficult to mix in the lab or field, producing a turbid, white solution resistant to injection operations. ACH exhibited the best properties during lab studies, displaying over 90 percent adsorption to PAS aquifer sediments. XRD studies showed that clay minerals conditioned with ACH formed a strong aluminous interlayer in sodium (Na) smectite clays, resistant to cation exchange, reactions with glycol and heating. By comparison, clay minerals treated with AlCl3 displayed no structural change, but showed evidence that Al+3 exchanged with Na+1 in the structure of Na-smectite.

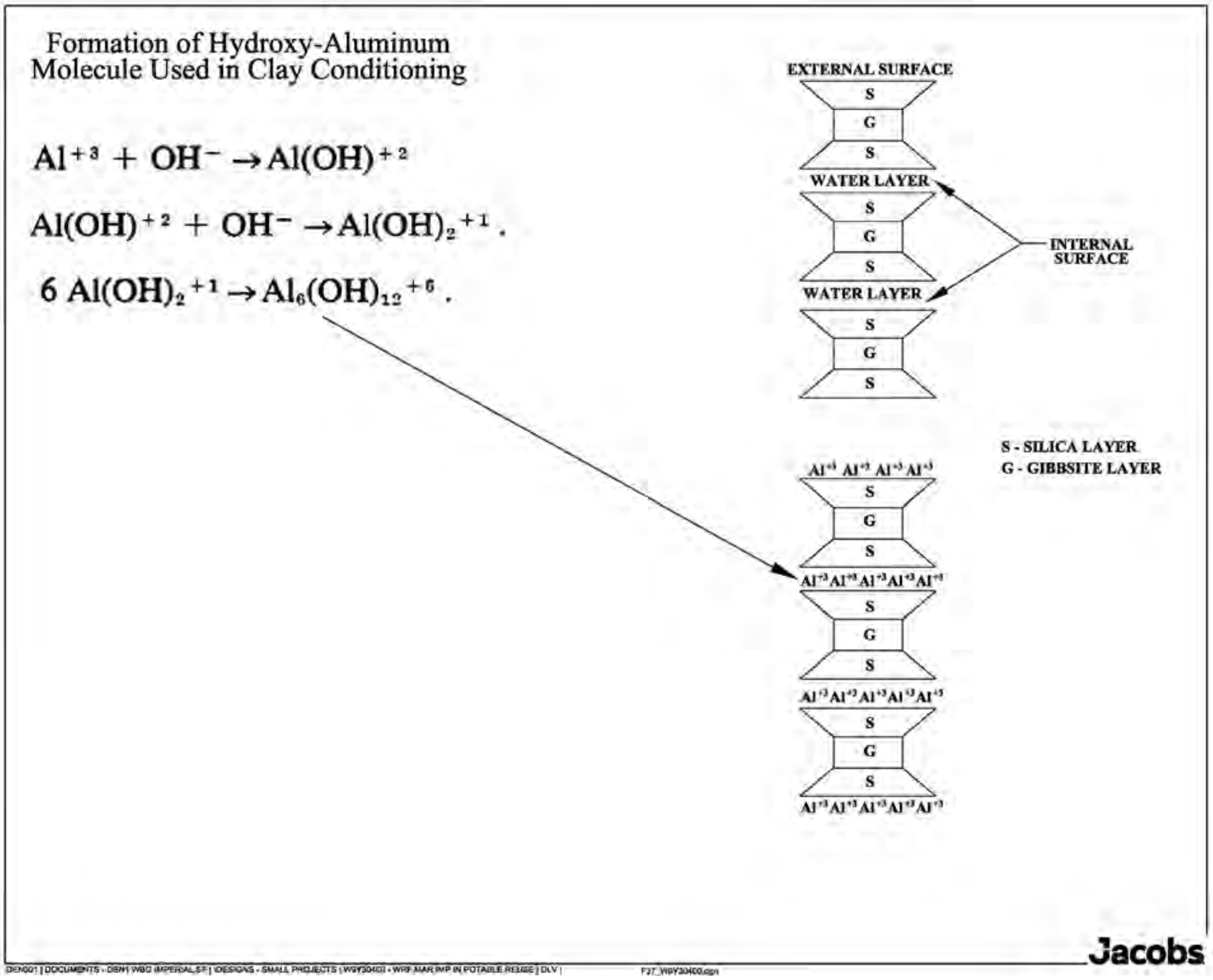


Figure C-30. Conceptual Diagrams of Conditioning Clay Minerals with Al-Salts.

C.3.2.2 Aquifer Conditioning

Screen intervals were isolated in groups of two, using packers. HRSD calculated the ACH solution volumes based on a conditioning a radius extending 14-feet into the PAS surrounding TW-5 (Table C-7). To preclude promoting elevated screen exit velocities, HRSD maintained the injection of treatment solution below 50 gpm. After a two-week residence time in each zone, HRSD pumped the spent treatment solution out of TW-5, using packers in the same interval sequence as conditioning, at rates exceeding 60 gpm.

Table C-7. Summary of ACH Volumes Used at HRSD VIP_SWIFT.

		Screen Depths (fbg)		Total length of screen	Treatment Radius	Volume treatment fluid	Total length of zone	Volume of water to evacuate zone & piping	Volume ACH	
Aquifer	Packed Zone Number	Top	Bottom	(ft)	(ft)	(gallons)	(feet)	(gallons)	(gallons)	(totes)
Upper Potomac	1	724	765	76	14	104,993	86	340	2951	12.3
		775	810							
	2	855	935	116	14	160,253	161	557	4504	18.8
		980	1016							
Middle Potomac	3	1112	1144	90	14	124,334	130	517	3494	14.6
		1184	1242							
	4	1280	1304	59	14	81,508	95	453	2291	9.5
		1340	1375							
Lower Potomac	5	1442	1458	68	14	93,941	100	492	2640	11.0
		1490	1542							
	6	1580	1615	70	14	96,704	95	501	2718	11.3
		1640	1675							
	7	1760	1776	36	14	49,734	100	543	1398	5.8
		1840	1860							

AlCl3	0.1 M	
Porosity	0.3	fraction
Porosity	30	percentage
Volume of 8-inch pipe	2.61	gal/ft
Volume of 2-inch pipe	0.16	gal/ft
Tote volume	240	gal/tote
Mixing ratio	29	gal of ACH per 1,000-gal solution

Total Treatment fluid (gallons)	711,466	gallon
MINUS ACH volume	20,590	gallon
Treatment fluid minus ACH (gallons)	690,876	gallon
ACH volume needed (gallons)	19,994	gallon
No. of totes	83	

C.3.2.3 Hydraulic Testing

To track the hydraulic performance of TW-5 during the conditioning process, step drawdown tests (step tests) were conducted prior to ACH conditioning (pre-conditioning), immediately following ACH treatment (post-conditioning) and after running a 72-hour injection test (post-injection). In conducting the post-conditioning and post-injection tests, HRSD reproduced the pumping rates (400, 500, 600, and 700 gpm) and step durations (60 minutes) employed during the pre-conditioning step test.

A 72-hour injection test was conducted from January 15 to 18, 2020, injecting 432,000 gallons of potable water into TW-5 at a consistent rate of 100 gpm. Potable water originated from a hydrant adjacent to the TW-5 site and displayed an ionic strength of 0.003 m/L, significantly below the ionic strength of the expected recharge at VIP_SWIFT. Most importantly, the injection volume exceeded the treated volume by 1.5 times, so the injection volume extended beyond the treatment envelope surrounding TW-5.

The higher injection test volume supported examining the hydraulic effects of pushing fresh water into untreated areas of the aquifer. Conditioning areas surrounding the wellbore protects the small surface areas susceptible to clogging. With distance from the MAR well, surface areas increase geometrically, thus, the intrinsic permeability of aquifer becomes less sensitive to clogging by dispersed clay minerals and fragments.

The specific capacity averaged approximately 9 gpm per foot of drawdown (gpm/ft) over the four steps of the pre-conditioning step test, but the average declined to 6 gpm/ft during the post-conditioning step test (Table C-8) a 33 percent drop attributed to the conditioning. Step test results following conditioning with Al-salts can range from modest improvements to measurable declines. Strengthening of inter-particle or interlayer attachments with Al-salts reduces the clay particle size while increasing interstitial pore space, improving the intrinsic permeability of the aquifer and subsequent well hydraulic performance. Conversely, flocculating clay minerals in pore spaces can occlude pore throats, reducing the intrinsic permeability of the wellbore environment. The losses experienced at TW-5 suggest clay particles flocculated in pore spaces despite HRSD’s best efforts to maintain injection rates during conditioning.

Table C-8. Summary of Step Drawdown Tests.

Results from HRSD VIP_SWIFT TW-5.

Test	Date	Specific Capacity (gpm/ft)
Baseline	6-Aug-19	8.97
Post-Conditioning	14-Jan-20	6.06
Post-Injection	21-Jan-20	4.78

C.3.2.4 Injection Testing

The injection level in TW-5 rose (draw-up) 44 feet over the 72-hours of the injection test (Figure C-31). Most of the draw-up (35 feet) occurred over the first day of the test. Most importantly, no noticeable inflective increase in draw-up was observed after recharge migrated beyond the treatment envelope, estimated around 2,800 minutes into the test. Indeed, draw-up increased less than four feet over the final day of the test

The specific capacity during the post-injection step test averaged 4.8 gpm/ft, a decline of around 20 percent compared with results from the post ACH test (6 gpm/ft; Table C-8). ASR wells screened in the PAS that have undergone conditioning with Al-salts in New Jersey and Delaware exhibited similar injectivity declines upon initiating recharge operations. The decline originates from several factors including clogging from TSS entrained in the recharge, particle re-arrangement when transitioning from a development program based on pumping to recharge, and mild clay dispersion in interstitial areas not reached during treatment.

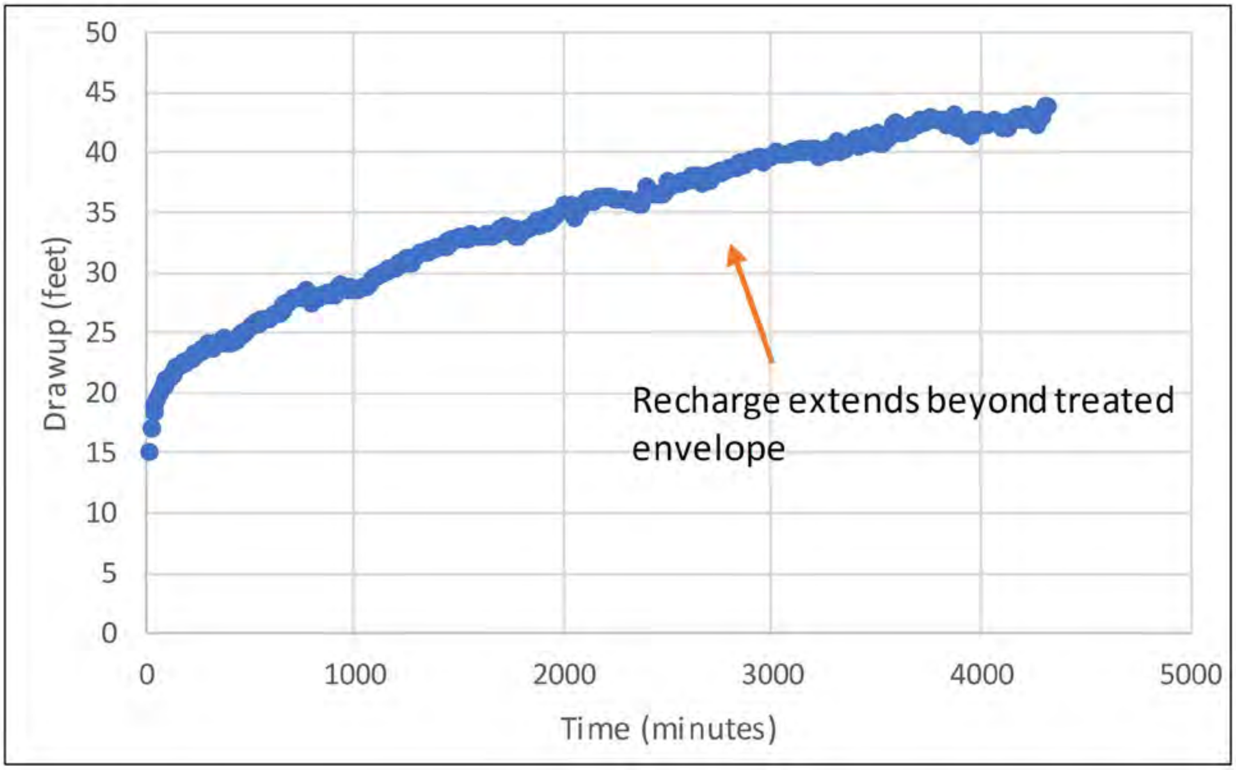


Figure C-31. Drawup During Post-Conditioning 72-Hour Constant Rate Injection Test at TW-.

Appendix D

Decision Framework Tool

D.1 Approach and Methodology

An interactive DFT was developed in conjunction with the overall Decision Framework under Task 4 of this project. The primary objective of the tool was to transform the Decision Framework into an interactive resource that steps the user through the series of questions related to Phase 1, Phase 2, and Phase 3 MAR evaluations, as described in Chapter 4. The intended outcome of the tool is to provide utilities with an additional resource to help them evaluate potential physical and geochemical issues anticipated when applying potable reuse for MAR to basins or wells.

The project team sectioned the Excel-based DFT into three hierarchical topics and seven secondary topics to capture the main process pathways of the Decision Framework as well as the secondary flow charts, case studies, and salient literature. The DFT utilizes different tabs for each topic listed below:

- Hierarchical topics:
    - Phase 1—Fatal Flaws Analysis
    - Phase 2—Geochemical Field Investigation
    - Phase 3—MAR Facility Start Up and Operations from a Geochemical Perspective
- Secondary topics:
    - Ionic strength
    - Clay conditioning
    - Arsenic mobilization
    - Cationic metals
    - Formation sampling
    - Cold recharge water
    - MFI testing

The tool steps the user through the three hierarchical topics (Phase 1, Phase 2, and Phase 3 of the Decision Framework) and provides catered resources (secondary topics) based on the selected inputs. The tool augments internal information stored within by guiding the user to references contained in the appendices and the comprehensive bibliography of the report. The tool incorporates a methodical, user-friendly design, which requires no specialized experience with Excel.

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