

Technical basis for the use of Sulfur-Modified Iron (SMI) for removal of selenium from coal mine waste waters

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For SMI Inc.

Executive Summary

Sulfur modified iron (SMI) is a reactive media for removal of contaminants from water that is very effective at removing selenium. The media is composed of iron and sulfur that has been hydrothermally pre-reacted and granulated for use. During feed water treatment, SMI reacts slowly with water to cause the formation of alteration minerals that selectively extract selenium and other toxic species from the water and incorporate them into their crystal structures. In this process the soluble selenium is generally reduced to well below the MCL. SMI is preferred over other reactive media such as zero-valent iron (ZVI) because it removes selenium to lower levels, is better able to maintain its permeability during use, has less effect on fluid pH, and once loaded is less susceptible to selenium release. It is preferred over sorbing media such as iron hydroxides because of its higher selenium uptake capacity, the ability to remove selenium to lower levels, no negative affect from soluble sulfate or arsenate, its ability to remove selenium in all common oxidation states, and a greater capacity of used media to retain selenium.

Background

Selective removal of water contaminants such as selenium is often carried out using sorbing materials and ion exchange resins (Faust and Aly, 1997; Westerhoff, 2003; Daus et al., 2004). Ion exchange resins are generally re-cycled through regeneration using a concentrated salt solution. A secondary waste stream is produced in the process. Sorbing media are generally used just once and disposed of in a landfill provided they pass the appropriate leach tests. The sorbants generally target one species (Clifford, 1990). For example, engineered ferric hydroxides have been developed for removing selenium from water supplies that operate by sorbing negatively charged selenate onto a precipitating positively charged ferric hydroxide surface (EPA, 1990; Golder and Associates, 2009).

Reactive media are also used to remove contaminants. Reactive media remove the contaminant via a chemical reaction, unlike sorbants which remove the contaminant by sorbing (coating) it onto a mineral surface. Zero-valent iron (iron in metallic form) is the most common reactive media and is effective for removal of arsenic, selenium, mercury and other metals (Han, 2009). Reactions between water and iron cause formation of new solid phases that either co-precipitate with the contaminant, or the contaminant sorbs to the mineral surface and is removed from solution (Liang et al., 2005). Because of the reaction, the removal capacity of reactive media per gram of material is usually much larger than that of simple sorbing media.

Non-selective desalination technologies such as reverse osmosis and electrodialysis can also be used to remove contaminants. They are less desirable because they remove other dissolved

species in addition to the contaminants of interest, at a significant cost penalty. Unless there is a need for both desalination and toxic species removal, these technologies are rarely cost-effective (EPA, 2000).

Sulfur-modified iron (SMI)

Sulfur modified iron (SMI) can be thought of as an improved type of zero-valent iron (ZVI) media to which a few weight percent of elemental sulfur has been added. The two solids (iron and sulfur) are partially reacted in water at elevated temperature to form alteration phases that include iron sulfides, mixed-valent iron oxides, and iron hydroxides, as well as residual iron and sulfur (Table 1). The alteration phases are important for enhancing contaminant removal because the contaminants present in the feed water become incorporated into these phases as they continue to grow during treatment.

Table 1. Some likely reactions in SMI media involving iron, sulfur, selenate and their reaction products

$\text{Fe}^0 + 2\text{H}^+ + \frac{1}{2} \text{O}_2(\text{aq}) = \text{Fe}^{++} + \text{H}_2\text{O}$	
$\text{Fe}^0 + \frac{3}{4} \text{O}_2(\text{aq}) + 1.5 \text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s})$	
$\text{Fe}^0 + \text{S}^0 = \text{FeS}$	
$\text{Fe}^0 + 2\text{S}^0 = \text{FeS}_2$	
$\text{S}^0 + \text{H}_2\text{O} + \text{Fe}^{++} = \frac{1}{2} \text{O}_2(\text{aq}) + 2\text{H}^+ + \text{FeS}$	
$\text{S}^0 + \text{H}_2\text{O} + \frac{3}{2} \text{O}_2(\text{aq}) = 2\text{H}^+ + \text{SO}_4^-$	
$6 \text{Fe}^{++} + \text{HCO}_3^- = \frac{1}{2} \text{O}_2(\text{aq}) + 13 \text{H}_2\text{O} = 11 \text{H}^+ + \text{Fe}_6(\text{OH})_{12}\text{CO}_3 \cdot 2\text{H}_2\text{O}$	(Carbonate Green Rust)
$\text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} = \text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2 + 6\text{H}^+$	(Jarosite)
$\text{KFe}^{3+}_3(\text{OH})_6(\text{SeO}_4)_2$	Selenate-Jarosite endmember
FeSe_2	Ferroselite (pyrite analog)
FeSe	Achavalite (pyrrhotite analog)

SMI has some key advantages with respect to ZVI and other selective removal technologies. Field tests show that, when compared to zero-valent iron, SMI has greater longevity, releases less iron, remains more permeable, and has less effect on pH. In addition, in sulfate-rich waters, which are common in coal mine waste waters, the SMI reacts with the sulfate in the water to form Jarosite ($\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$) which has a high affinity for selenium as selenate (SeO_4^-) in its crystal structure (Fig 1). The selenate replaces sulfate in the structure which allows the SMI to remove essentially all the selenium present, often to below detection limits. Also, the selenium is fixed in the mineral phase and therefore is very resistant to later leaching, for example in a landfill.

Both SMI and ZVI are reactive media so that they continue to react over time and have a much higher overall capacity for selenium removal than a sorbing media such as iron hydroxide (Wilkin and Puls, 2003). Once coated to capacity, sorbers stop removing the toxic species and in fact under some conditions can start releasing it back into the environment (“chromatographic peaking”). Both SMI and ZVI have the advantage that selenium removal is aided by the

presence of sulfate, in contrast to sorbing media which are generally negatively impacted by and lowers selenium removal capacity.

Tests show that ZVI tends to raise the pH of the treated water more than SMI (Santina, 2003). This is generally undesirable because it can result in the precipitation of carbonate and sometimes silica scale, which harden or clump the media and reduce both its permeability and reactivity. The difference in pH effect can be explained as a consequence of the acidity balance of the reactions involving both sulfur and iron in SMI media as compared to iron alone in ZVI (Table 1 above shows pH-dependent reactions involving sulfur and iron precipitates). With the SMI media, the precipitation of iron-sulfur phases instead of iron hydroxide phases reduces the overall consumption of acid and reduces the rise in pH vs. that for ZVI.

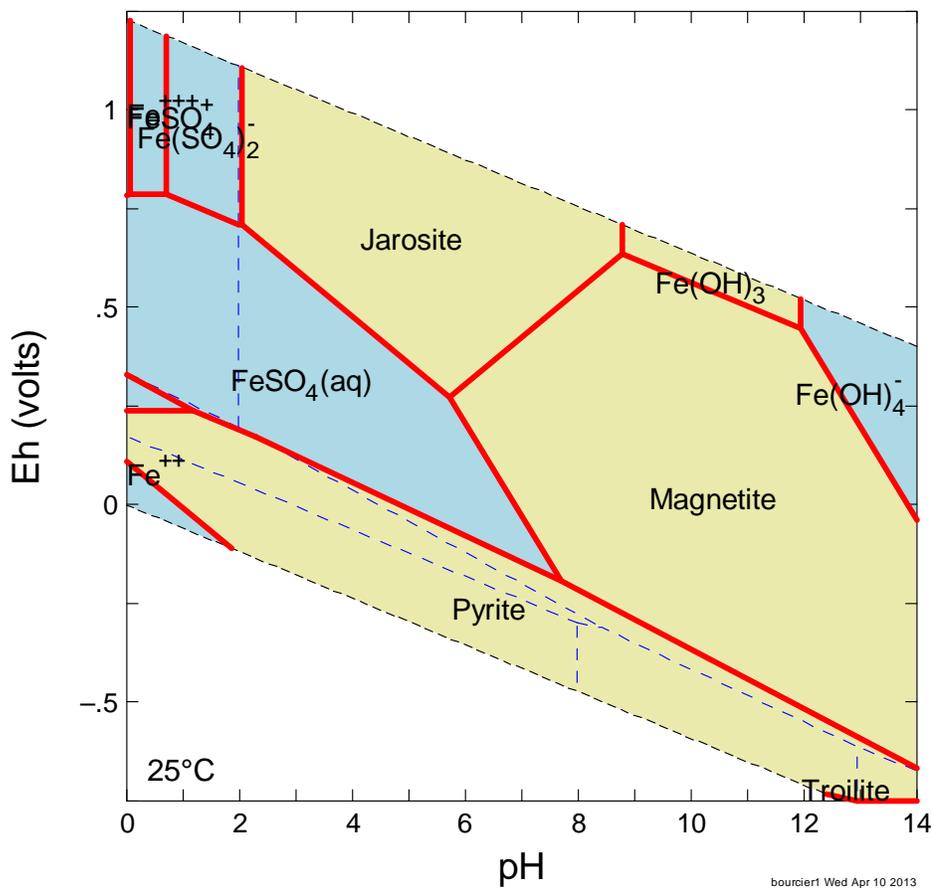


Diagram Fe⁺⁺, T = 25 °C, P = 1.013 bars, a(H₂O) = 1, a[H⁺] = 1, a[SO₄⁻²] = 1 (precipitates), Suppressed: Hematite, Goethite

Figure 1. Phase stabilities in the iron system as a function of oxidation state (Eh) and pH. The tan regions show solid phase stabilities and the blue fields show aqueous phases stabilities, with boundaries at 0.1 mmolar total iron. Selenium solubility is particularly low in the regions of stability of Pyrite and Jarosite. The Eh-pH conditions where these two phases are stable are targeted in the SMI synthesis process to optimize SMI for selenium removal from the feed water.

SMI releases less dissolved iron into the water supply than does ZVI. Testing has shown that soluble (ferrous) iron is generally lower for tests involving SMI (California Water Services, 2002; Schreier, 2002, 2003, 2004, 2005) than for tests involving ZVI (Ruangchainikom et al., 2006; Westerhoff and James, 2003; Wilkin and McNeil, 2003). Iron concentrations between 1 and 10 ppm are typical for SMI tests whereas iron concentrations of several hundred ppm are observed in many ZVI tests.

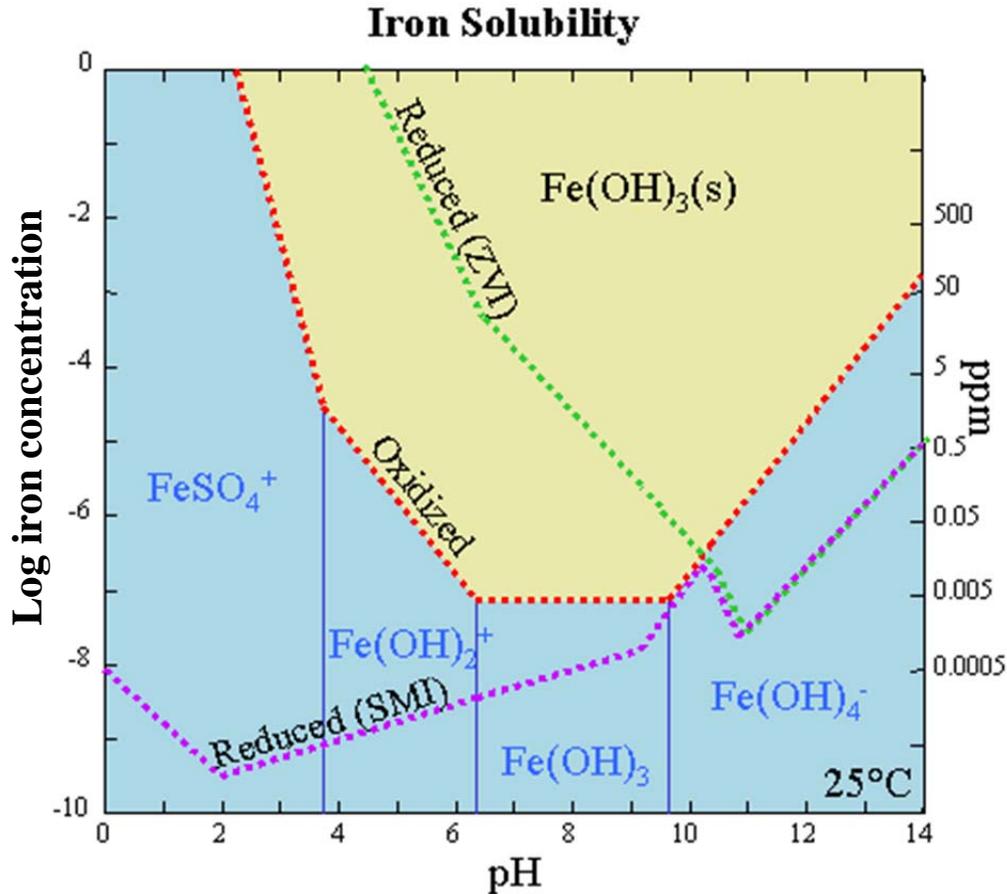


Figure 2. Solubilities of iron vs. pH under reducing conditions in equilibrium with SMI (purple) as compared to ZVI (green), and for both media for oxidizing conditions (red) as a function of pH. Note that SMI has much lower iron solubility under reducing conditions and will therefore release less iron into the water supply. The sulfur added in the synthesis of SMI causes the formation of sulfur and iron containing solids that lower iron solubility.

A likely reason for SMI’s lower iron release is shown in Figure 2 where iron solubilities for ZVI and SMI are compared as a function of pH and redox states¹. The green curve shows that for reducing (anaerobic) conditions, ZVI without added sulfur is fairly soluble (>1 ppm below pH 8) whereas by adding sulfur (SMI - purple curve) the iron remains insoluble at low pH values due

¹ Calculations carried out using the “Act2” code of The Geochemist’s Workbench version 4.0. Data for carbonate and sulfate “green rust” phases that control iron solubility at neutral pH were added using thermodynamic data from Bourrie et al., 1999.

to formation of low-solubility iron sulfide phases. For oxidizing conditions (red curve) iron solubility for both ZVI and SMI is controlled by ferric hydroxides and remains low (<1 ppm) down to about pH 4. During service conditions, the redox state will vary between reducing and oxidizing in a complex way and in general allow much more iron release from ZVI than from SMI. The stabilities of iron phases considered in this calculation are shown in Figure 3.

Selenate (the anionic form of selenium stable in solution in contact with air) is readily incorporated into several of the reaction products. It can be in the interlayer (anionic) sites in the “green rust” phase that forms from reaction of ground waters with iron. It also is known to substitute into the structures of both iron sulfide (pyrrhotite) and iron disulfide (pyrite) phases. In fact, it is known to occur in nature as a pure FeSe_2 phase where the S_2^{2-} sulfur group (disulfide) is completely replaced by selenium. Under more oxidizing conditions with sulfate present, it will replace sulfate in the mineral Jarosite (stability shown in Fig 1.) Compositions of these phases are shown above in Table 1.

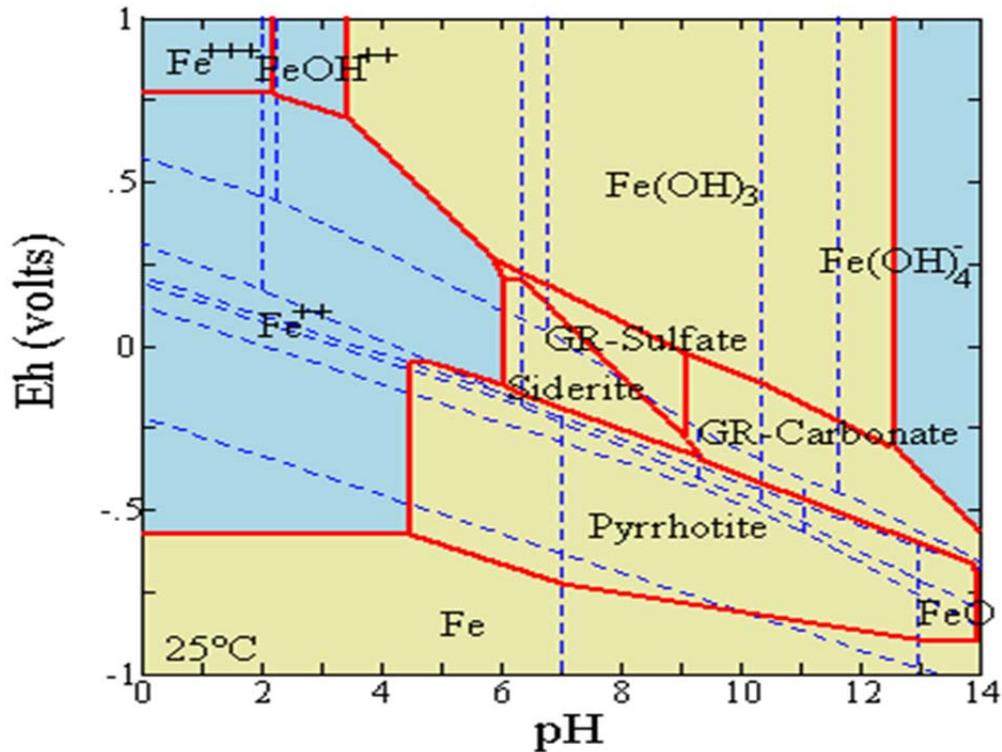


Figure 3. Stabilities of iron phases considered in calculation of iron solubilities in presence of SMI and ZVI media. “GR” refers to the “green rust” phase observed as an alteration product of ZVI in groundwater. Pyrrhotite is an iron monosulfide phase ($\text{Fe}_{(1-x)}\text{S}$) that is used as a proxy for the iron sulfide reaction products in SMI.

For water treatment and for later landfill disposal of the spent media, it is important to know whether selenium is mainly sorbed onto a mineral surface, or is more irreversibly sequestered internally into a mineral phase. If selenium is contained within a mineral phase it is much less susceptible to rapid and wholesale release during “chromatographic peaking” which can occur,

for example, with sorbing media. Chromatographic peaking occurs when a media becomes saturated with sorbing species and where continued use causes the more weakly sorbing species to be exchanged for more strongly sorbing (e.g. phosphate or sulfate for arsenate on iron hydroxides). The process may result in a detrimental rapid release of toxic species to the water supply.

In addition, in the case of disposal of spent media in a landfill, the material is much more likely to pass the required leach tests (e.g. TCLP) if the selenium is within mineral phases than if it is sorbed onto their surfaces. The acids present in the TCLP leach solution are generally not able to dissolve mineral structures and release the contained selenium, whereas the acids may be able to release selenium sorbed to mineral surfaces.

Note that SMI is also effective at removing other contaminants potentially present in the coal mine waters, in particular arsenic and mercury (Han, 2009; also true for ZVI). Use of SMI therefore acts as a barrier to release of arsenic and mercury from the mine waste ponds into the environment, at no added cost.

We are aware that microbes could be involved in the selenium capture processes taking place during the use of the SMI media. Both anaerobic and aerobic bacteria are known to take advantage of redox disequilibria to supply their energy requirements (Beller et al., 2005). Although conditions during treatment of coal drainage waters are not optimal for biological activity, it is possible that bacteria may be actively using the energy supplied via iron oxidation for their metabolic needs. Whether or not the microbes are present, their activity will most likely only speed up the iron oxidation reactions which are known to give rise to selenium removal from the feed water, and not interfere with selenium removal.

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ADDITIONAL UNPUBLISHED REFERENCES

In cooperation with Prima Environmental, the inventor (PS) has carried out previous work to test the SMI media for water treatment applications. These studies have resulted in the following unpublished reports:

“Evaluation of field pilot tests for nitrate removal by SMI-III. Letter report to Chet Aukly of California Water Service Company from Cindy Scheirer of Prima Environmental, July 7, 2003.

“Evaluation of SMI-III for removal of hexavalent chromium from groundwater, McClellan AFB, California, from Cindy Scheirer, Prima Environmental to Peter Santina, SMI, Inc.

“Report of findings: Removal of nitrate from drinking water using sulfur-modified iron (SMI). Unpublished report from Prima Environmental, July 2001.

Technical review of field pilot testing for the removal of nitrate from drinking water by sulfur modified iron (SMI). Unpublished report from Prima Environmental, October 2003.

In addition, other workers have reported on the use of SMI for water treatment applications. A partial listing of those reports includes:

City of Ripon, California, Proposition 50 Project “Integrated Nitrate and Arsenic Treatment Demonstration – Final Report ID No. P50-3910007-055, February 2010.

“Arsenic removal testing – Phase I and II Report”, unpublished letter report from Dr. Paul Westerhoff of Arizona State University to Michelle De Haan of Damon S. Williams Associates.

“Sulfur modified iron (SMI) for the removal of arsenic from water”. M.S. thesis by Janet M. Thomas, University of Nevada at Reno. May 2000.

“Pilot testing of iron-based sorption media for arsenic removal in waters with high and low silica levels”, Unpublished Powerpoint presentation of Erin McCauley of California Water Services Company. February 2003.

“Adsorptive media experiments”, Unpublished Powerpoint presentation by Dr. Chad Seidel and others of McGuire Environmental Consultants, 2005.

Biographical sketch for William Bourcier:

William Bourcier until recently was a staff research chemist in the Energy and Environment Directorate at Lawrence Livermore National Laboratory. At LLNL he led or assisted with several water treatment and water desalination projects at bench to pilot scale, including a novel electrostatic desalination technology, a carbon dioxide separation technology based on conventional desalination, and a membrane-based method for producing marketable silica from geothermal fluids. Previous to this, he spent over a decade working on the development of durable glass and ceramic waste forms for radioactive waste disposal. He also worked on projects to measure thermodynamic properties of aqueous systems, including mineral solubilities and stabilities of aqueous species at elevated temperatures. He currently serves on technical review boards overseeing water treatment and water use technologies related to cleanup and power generation sponsored by the Electric Power research Institute, the California Energy Commission, the California Department of Water Resources, and others. William left LLNL in 2008 to co-found Simbol Mining Corporation (now Simbol Materials), a company focused on developing and implementing extraction technologies to harvest marketable by-products from aqueous brines. He recently returned to LLNL part-time to work on water-related and other aspects of geologic sequestration of carbon dioxide. William received his Ph.D. in Geochemistry&Mineralogy from Penn State University in 1983 with a thesis on the origin of hydrothermal mineral deposits and the chemistry of hydrothermal fluids.

Curriculum Vitae for
William L. Bourcier, Ph.D.

PRESENT POSITION:

Chemist/Materials Scientist (half-time retiree)
Lawrence Livermore National Laboratory
Livermore, CA 94550, (925) 422-9885
wbourcier@gmail.com, bourcier1@llnl.gov

Other activities:

- National Laboratory Liaison Consultant to Campbell Applied Physics, Robert Campbell, CEO
- Over the last two years I have had consulting contracts with Toray Membranes, NanoH2O, Professional Water Technologies, Calera Corporation, The California Energy Commission, U.S. Bureau of Reclamation, and the U.S.EPA
- Fellow at the Center for Integrated Water Research, University of California at Santa Cruz, Brent Haddad, Director

SUMMARY: I have broad experience in materials science, working on and leading R&D projects in the areas of:

- Development and testing of desalination and selective extraction water treatment technologies
- Carbon dioxide capture using aqueous and enhanced amine-based processes
- Solution mining of metals from saline fluids
- Ceramic, glass, and metals corrosion
- Reactive transport modeling of aqueous systems
- Measurement of thermodynamic data for aqueous systems

CURRENT PROJECTS AT LLNL:

- Water issues related to geologic sequestration of carbon dioxide from fossil fuel plants.
- Carbon capture and storage using synthetic enzymes and encapsulated solvents.
- Developing a technology for using colloidal silica as a geological reservoir blocking agent and zonal isolation material.

MOST RECENT PROJECT: Worked as part of a team to develop and implement extraction technologies for metals and other marketable by-products from geothermal and other types of aqueous fluids (while R&D Director at Simbol Mining Corporation)

RESEARCH PROJECTS WHILE EMPLOYED AT LLNL

- P.I. of pilot project to extract marketable metals and commodities from geothermal fluids at Mammoth Lakes California. Co-funded by the California Energy Commission and DOE-Geothermal (\$700K over 2 years).
- P.I. of project to develop element-selective electrodialysis membranes for treatment of impaired water. Funded by California Dept. Health Services, \$2.1M planned for 2009-2012.
- P.I. of project to develop a low-energy desalination process ("ion pump") using electrostatic fields. Funded by California Dept. Water Resources, \$1M over 2006-2009.

- P.I. of internally-funded (LDRD) project “Nanofilters for metal extraction” developing functionalized silicon/alumina membranes to concentrate arsenic for arsenic sensor (\$175K).
- Co-P.I. on EPRI project to investigate water-based carbon dioxide separations technologies.

PREVIOUS EXPERIENCE:

March 2008-May2009, Director of Research & Development, Simbol Mining Corporation, Pleasanton, CA

January 1985-March 2008, Staff Chemist, Lawrence Livermore National Laboratory, Livermore CA. Geochemistry Group Leader, August 2007-March 2008.

EDUCATION:

1983--85 National Research Council Post-Doc, NASA, Johnson Space Center

1977--83 Ph.D. in Geochemistry and Mineralogy, Pennsylvania State University

1972--77 B.S. in Geology, Oregon State University

INTELLECTUAL PROPERTY:

US 20120273359 A1 “Flow-through electrode capacitive desalination” Inventors M. Suss, M. Stadermann, C. Spadaccini, K. Rose, W. Bourcier, T. Baumann, and J. Santiago

IL-12326 “Use of colloidal silica as a blocking agent, zonal isolation material, and fast-path blocker in geologic reservoirs”, Inventors W. Bourcier, S. Ezzedine, S. Roberts, Jon Hunt, and J. Roberts.

IL-11902 “Silica extraction from geothermal water”, Inventors, W. Bourcier and C. Bruton (Patent applied for)

IL-11609 “Desalination using electrostatic ion pumping” Inventors: W. Bourcier, R. Aines, J. Haslam, C. Schaldach, and K. O’Brien, Patent Application, Date: 1/30/2006. (Patent applied for)

IL-11301 “Computer designed nanoengineered materials for separation of dissolved species” Inventors: W. Wilson, C. Schaldach, W. Bourcier, and P. Paul Date: 11/30/2003 (Patent Approved)

IL-11462 “Hybrid electrodialysis approach for selective removal of contaminants” Inventors: J. Haslam, W. Bourcier, and K. O’Brien

IL-11302 “Smart membranes for nitrate removal, water purification, and selective ion transportation”, Inventors: W. Wilson, C. Schaldach, W. Bourcier, and P. Paul. Patent Approved.

IL-1169 “Nanoengineered field induced charge separation (FIC) membranes for water purification”, Inventors K. O’Brien, J. Haslam, and W. Bourcier

IL-11566 “Carbon ion pump for removal of carbon dioxide from combustion gas and other gas mixtures”, Inventors Roger Aines and William Bourcier. (Patent applied for)

PUBLICATIONS

Book Chapters:

Bourcier, W. L. and K. Sikafus (2006) Storing waste in ceramic. Chapter 26 in Uncertainty Underground, Allison Macfarlane and Rodney Ewing, editors. MIT Press.

Bourcier, W.L., and Barnes, H.L. (1987) Rocking autoclaves for hydrothermal experiments I. Fixed volume systems. In G.C. Ulmer, and H.L. Barnes, Eds. Hydrothermal Experimental Methods, p. 189-215. John Wiley & Sons, New York.

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Papers:

W.L. Bourcier, T.J. Wolery^a, T. Wolfe^b, C. Haussmann^c, T.A. Buscheck^a, and R.D. Aines^a (2012) A preliminary cost and engineering estimate for desalinating produced formation water associated with carbon dioxide capture and storage. *Nt. J. Greenhouse Gas Control* 5:1319-1328.

Matthew E. Suss, Theodore F. Baumann, William L. Bourcier, Christopher M. Spadaccini, Clint A. Rose, Juan G. Santiago and Michael Stadermann (2012) [Capacitive desalination with flow-through electrodes](#) *Energy Environ. Sci.*, DOI: 10.1039/C2EE21498A

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