

# BIOREMEDIATION OF GROUNDWATER CONTAMINATED BY PHOSPHATE MINING AND EXTRACTION: A NEW APPROACH USING INDIGENOUS SULFATE-REDUCING BACTERIA

by

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**Abstract.** Groundwater in west central Florida is locally contaminated by sulfate ( $\text{SO}_4$ ), calcium (Ca), iron (Fe), heavy metals, and uranium decay-series radionuclides, which are byproducts of phosphate production. Waste solution from phosphate extraction and fertilizer production is discharged to evaporation ponds creating approximately 30 million tons of gypsum waste each year. About 1 billion tons are currently stored above ground in Florida. Especially problematic are older gypstacks that were mixed with mine tailings, thus accelerating leaching of Ca,  $\text{SO}_4$ , Fe, U, and radionuclides to groundwater. Artificial stimulation of metabolism of indigenous sulfate-reducing bacteria (SRB) has the potential to remediate groundwater impacted by phosphate mining and extraction. This sulfate reduction technology takes advantage of anaerobic heterotrophic bacteria already present, though it requires that nutrients be present to stimulate metabolism. Soluble organic carbon required by the bacteria is generally lacking and will have to be injected into the subsurface in planned future studies. However, geochemical reactions attending biogenic sulfate reduction can be modeled using a thermodynamic reaction path computer program, PHREEQC. Model results indicate that sulfate reduction can remove contaminants from groundwater to within or near federal and state drinking water standards. The SRB simultaneously oxidize organic carbon to bicarbonate and reduce the sulfate to hydrogen sulfide ( $\text{H}_2\text{S}$ ). Sulfate reduction can produce many beneficial results, such as an increase in pH and alkalinity and an overall decrease in total dissolved solids (TDS). These effects are facilitated by the precipitation of Ca,  $\text{SO}_4$ , Fe, U, and As as relatively insoluble mineral phases, such as As-rich pyrite. The presence of indigenous sulfate-reducing bacteria in gypstacks and groundwater, ambient geochemical conditions, and thermodynamic modeling results all suggest that a controlled stimulation of SRB metabolism is a viable remediation technology for groundwaters adversely impacted by gypstacks in central Florida.

Additional Key Words: sulfate-reducing bacteria, in-situ bioremediation, sulfide minerals

## Introduction

Phosphate mining is a large industry in central Florida, accounting for about 25 percent of the world's fertilizer production. The ore consists of Miocene calcium-phosphate-bearing clays (e.g., the mineral apatite), which is subsequently dissolved in sulfuric acid. Commercial products (either diammonium phosphate or phosphoric acid) are produced from that solution (Figure 1) (Burnett et al., 1995). The remaining phosphate-depleted solution is pumped to ponds and evaporates to form the mineral gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). This gypsum is referred to as "phosphogypsum" and builds up to form "gypstacks" as the dikes, which form the ponds, are raised.

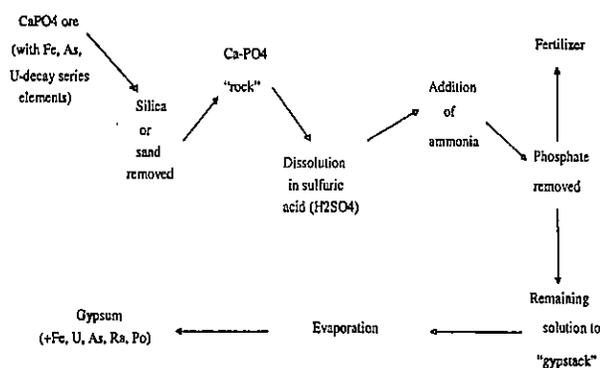


Figure 1. Schematic flow chart of the phosphate mining and extraction process

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Some gypstacks in central Florida are as high as 24 meters, and approximately one billion tons of phosphogypsum are stored in Florida in this manner. Furthermore, approximately 30 million tons of new phosphogypsum (3 tons produced for every ton of fertilizer) accumulate every year.

Phosphogypsum can not be used for most commercial applications because the gypsum contains

traces of naturally-occurring radioactive materials (NORM) produced by the decay of uranium that was originally present in the phosphate ores. In particular, radon gas is problematic. In the past several decades, gypstacks have been required to have a liner present at their bottom, which has mitigated against any significant groundwater contamination around the newer gypstacks. However, older gypstacks were not required to have liners and also the gypsum was often mixed with mine tailings. These older gypsum accumulations have been subjected to rainfall-induced dissolution, and locally have contaminated shallow groundwater with Ca, SO<sub>4</sub>, Fe, some heavy metals, and radionuclides.

Recent regulatory decisions by the State of Florida require that groundwater contaminated by the older gypstacks be remediated. To date, some proposed remediation procedures have included treating the gypstacks (regrading and covering them with thick soil), doing a conventional pump-and-treat process on contaminated groundwater, and even constructing slurry walls to contain and stabilize the contaminated plumes. We have proposed (Saunders et al., 1997a, Whitmer, 1998; Whitmer and Saunders, 1999) that an in situ bioremediation process should be an effective and potentially very cost-effective way to remediate groundwater contaminated by phosphogypsum. In this paper, we present an overview of the hydrogeology, geochemistry, and geomicrobiology of one site in Florida and in the process demonstrate why we think this new type of bioremediation process will be effective. In addition, we discuss how this bioremediation can be accomplished from a technological standpoint.

### Geology and Hydrogeology

The P-21 study site is located 48 kilometers east of Tampa near Bartow, Florida and is within the Central Florida phosphate district. The physical appearance and subsurface geology of this area is characteristic of Florida. The relatively flat topography rises 50 to 130 meters above mean sea level in central Florida. Stratigraphy in this area consists of Pliocene-Pleistocene clastics, clays, and carbonates typical of a marine depositional environment.

There are three aquifer systems in the region: surficial, intermediate, and the Floridan aquifer, which is the main water-bearing unit (Whitmer, 1998). The intermediate aquifer is separated from the Floridan aquifer by the phosphate-rich semi-confining unit. The main phosphate-rich ore unit is the Miocene Bone Valley Formation, which also serves as a semi-confining unit in the aquifer system. Groundwater in

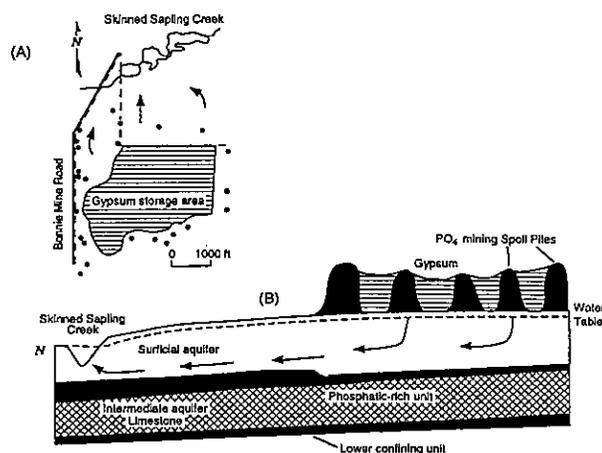


Figure 2a. Plan map showing the gypstack under study and placement of monitoring wells. Arrows show direction of water flow towards the stream. (from Whitmer, 1999)

Figure 2b. Diagrammatic cross section of the gypstack showing the mixture of sand tailings and gypsum and the general subsurface geology.

the region flows west and south (Southeastern Geological Society, 1977). Near the study area the flow also has a radial component due to the tendency of the water table to conform to the mounding of the gypstack as well as a northwest component of flow toward a small stream (Figure 2a). Within the system the flow is primarily horizontal because there is little to no vertical leakage between the layers (Florida State University, 1998).

The principal ore mineral, a carbonate rich apatite, is mined from the 10 to 20 meters of unconsolidated limestone in large-scale open pit operations. The ore is crushed, washed to remove silica, and then chemically treated to remove the phosphate. Mining pits are typically back filled and stockpiled topsoil is used to cover the reclaimed tailings.

The gypstack studied here covers about 4 square kilometers and rises 30 meters above sea level. This older gypstack was deposited during a time of less stringent regulations. It consists of a mixture of sandy mine tailings and gypsum and does not have a liner (Figure 2b). This gypstack is therefore more permeable and the aquifer below more susceptible to contamination. Over time, cracks have formed in the gypsum thus increasing the permeability. Rainwater can easily seep through this heterogeneous mixture of mine spoils and gypsum, allowing transport of leached SO<sub>4</sub>, Ca, Fe, and other contaminants into the underlying aquifer.

Elevated levels of Ca, SO<sub>4</sub>, heavy metals, and radionuclides locally contaminate the surficial aquifer.

The gypstack has high concentrations of trace elements (U and radioactive decay series elements), rare earth elements, and iron, which remain with the sulfuric acid solution after the fertilizer production process. Other environmental concerns are extremely high TDS and low pH. The contaminated water has five times the TDS standard for drinking water and 6 times the sulfate standard of 250 ppm. Dissolved iron in this groundwater is almost 70 ppm and the drinking water standard is 0.3 ppm. The pH of 5.1 is mildly acidic and obviously a cause for concern. The concentration of uranium in this groundwater was not analyzed but can be inferred to be high, as the concentration of Ra-226, a daughter element, is 10.8 pCi/l, which is more than twice the drinking water standard of 5 pCi/l.

Evaluating the geochemistry of the phosphate ores, mine tailings, and gypsum shows that most often trace elements are more concentrated in the ores themselves (Table 1). For example, uranium concentration in the ores varies between 79 ppm and 138 ppm as compared to about 20 ppm in the tailings and merely 2 to 4 ppm in the gypsum. The uranium and radioactive decay series elements that are inherited from the U-rich parent ore remain with the gypsum and prohibit industrial use of this byproduct. Instead, the gypstack was left on the surface, which led to the contamination problem existing today.

Other constituents in the ores, tailings, and gypsum also follow this trend. Comparison of the three reveals that there is about 35 percent Ca in the ore, 20 percent in the gypsum and 7 percent in the tailings. Similarly, the ore samples have two or more times the composite amount of some rare earth elements (La + Ce + Nd = 200 to 300 ppm) than the waste.

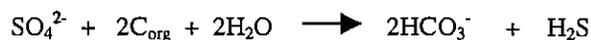
Because the groundwater potentially can derive solutes from both the gypsum and the phosphate ore, both have the ability to affect the trace element geochemistry. For this reason, it is likely that both sources control the overall geochemistry of the shallow groundwater, but the high levels of Ca, Fe, SO<sub>4</sub>, and low pH are due to leaching from the soluble phosphogypsum. The high levels of sulfate in contaminated groundwater provide the opportunity to try to stimulate naturally-occurring sulfate reducing bacteria to effect in situ bioremediation.

### Geomicrobiology of the site

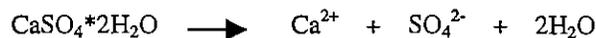
Although investigations on the geomicrobiology of the general gypstack environment in central Florida have been limited, these studies, along with the mineralogy and the geochemistry of the setting, provide clues as to expected geomicrobiological conditions. For example, gypsum is a fairly soluble

mineral, and if it is allowed to dissolve in pure water until local chemical equilibrium is established, then the water will contain at least 1,000 ppm dissolved sulfate. In nature, it is a general rule of thumb that there are sulfate reducing bacteria (SRB) wherever there is ample sulfate (e.g., Ehrlich, 1997). For example, marine deltaic and estuarine sediments in contact with seawater contain abundant SRB and rapid rates of biogenic, sulfate reduction (Jakobsen and Postma, 1994). SRB are technically strict anaerobes, but recent research indicates that they can create their own anoxic (reducing) microenvironment even under aerobic or oxygenated conditions (Jones et al., 1989).

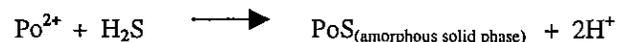
SRB are heterotrophic anaerobic bacteria that require a source of organic carbon for their metabolism. They couple the reduction of dissolved sulfate (instead of molecular oxygen like aerobes use) to the oxidation of the organic carbon and produce bicarbonate and hydrogen sulfide in the process:



Obviously, the more dissolved sulfate that is destroyed by the SRB, the more gypsum can be dissolved by the this reaction:



Burnett et al. (1995) cultured indigenous bacteria from the gypstack at the present study area to investigate microbiological controls on the release of contaminants to water. They were able to culture both aerobic and anaerobic consortia from the gypsum taken from the zone of aeration above the water table. They concluded that SRB were involved with the dissolution of gypsum and also indirectly with the subsequent release of contaminants contained in the gypsum. For example, one contaminant of interest, the radionuclide Po-210, was shown to be released to water in contact with gypsum containing the anaerobic bacterial consortium containing SRB. Burnett et al. (1995) also concluded that the amount of Po-210 liberated by the SRB due to gypsum dissolution would ultimately be limited by the formation of a Po-sulfide mineral by a reaction perhaps like this:



Groundwater at the site contains high levels of dissolved sulfate leached from the sulfate, as well as some metals and radionuclides as discussed above. Because previous investigations had focused on the geomicrobiology of the gypstack, we made an attempt to evaluate the geomicrobiology of the contaminated groundwater (Saunders and Whitmer, unpublished data). Initially, we had observed that two of the 10

Table 1. Geochemistry of phosphate ores and gypsum byproduct

Sample Number	Ore samples					Tailings	Gypsum Samples		
	1	2	3	4	5		6	7	8
Constituents in ppm									
As	5	5	5	7	7	<2	<2	<2	<1
Ca%	37.0	34.1	34.4	31.4	31.7	7.2	21.8	18.1	24.2
Co	5	3	4	6	8	2	<1	<1	1.8
Cr	51	51	50	50	45	20	<2	4	3.2
Fe	0.54	0.82	0.75	0.68	0.79	0.34	0.12	0.11	0.067
Na	0.13	0.33	0.36	0.30	0.42	0.08	0.03	0.03	292
Sb	4.8	1.7	1.8	1.6	1.4	5.5	0.2	<0.2	0.1
Se	21	<3	<3	<3	<3	4	<3	<3	<0.5
Th	3.6	7.9	7.0	6.3	7.3	4.6	1.1	1.6	0.9
U	138	94.6	79.1	82.4	117	19.8	1.9	3.0	3.8
Zn	188	92	126	85	85	47	<40	<40	13
La	64.1	91.5	88.1	87.7	88.3	24.4	30.9	17.8	28
Ce	82	121	108	115	131	39	43	26	39
Nd	50	80	63	74	80	18	26	11	21
Sm	8.6	12.8	11.6	11.3	12.0	3.9	4.6	2.4	3.93
Eu	2.4	3.5	3.1	3.2	3.4	1.0	1.1	0.5	0.99
Tb	1.9	2.6	2.4	2.3	2.2	0.6	0.7	<0.5	0.6
Yb	6.7	9.8	9.2	9.1	8.1	3.1	2.2	2.1	1.91
Lu	1.08	1.49	1.34	1.53	1.19	0.55	0.29	0.17	0.27

Concentrations are in ppm (except Ca)

Sample 1: Clear Springs, Hopewell Mine

Sample 3: IMC-180, 1960's ore

Sample 5: composite ore from district, 1998

Samples 7, 8, 9: gypsum samples randomly collected at the surface

Sample 2: composite of central FL ores, 1994

Sample 4: composite ore, NBS 120C

Sample 6: 1993 sand tailings

monitoring wells we sampled at the site had a distinct odor of H<sub>2</sub>S, the telltale indication of biogenic sulfate reduction. To further test this possibility, a polyethylene bailer rinsed in distilled water and nitric

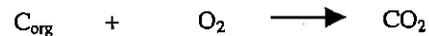
foot of the bailer (corresponding to the upper one foot below the water table) was bright orange from the presence of ferric hydroxide colloids forming under the most oxygenated conditions. A second bailer sample was used to fill anaerobic containers to which a water soluble organic carbon source was added and also to a control container to which nothing was added. Within one week internal pressure apparently produced from high levels of CO<sub>2</sub> gas broke the anaerobic seals and ended that part of the experiment before sulfate reduction began to produce H<sub>2</sub>S. However, within three weeks, SRB metabolism began in the control container, resulting in the formation of H<sub>2</sub>S and the precipitation of black iron sulfide colloids by the following reaction:



Thus, we concluded that enough organic carbon was present in the groundwater we sampled if the anaerobic conditions required to fuel biogenic sulfate reduction could be produced. Apparently, this reaction, mediated

acid was used to sample groundwater in an existing monitoring well at the site (which had no H<sub>2</sub>S smell). In the initial bailer sample, the water in the upper one-

by aerobic bacteria initially, led both to the breaking of the seals in our experiment and then ultimately to the anaerobic conditions in our control container:



In addition, from these experiments we have made an important conclusion relative to attempting bioremediation at the site. As long as the rate of oxygen consumption by aerobic bacteria exceeds the rate of oxygen diffusion from the atmosphere into groundwater, then anaerobic conditions suited for biogenic sulfate reduction can be maintained below the water table.

### Discussion

The current geochemical and geomicrobiological data from the site are indicative of sulfate reduction. The contaminated groundwater is mildly reducing below a depth of approximately one-

foot below the water table, which provides a suitable environment for the remediation. A limited amount of organic carbon is already present in the shallow groundwater. SRB from the site were cultured, which showed that they are common in the contaminated groundwater. Locally, the SRB are producing a limited amount of hydrogen sulfide where conditions are optimal. Furthermore, it is the minor amount of organic carbon present in the groundwater that currently limits extensive biogenic sulfate reduction at the site. Thus, in order to induce the indigenous SRB to remediate the contaminated groundwater in situ, additional organic carbon will have to be added.

Indigenous anaerobic bacteria generally can be thought of as competing with each other for terminal electron acceptors, organic carbon sources, and trace nutrients (e.g., Chapelle and Lovley, 1992; Chapelle, 1992; and Borowski et al., 1996). It is however the underlying thermodynamics that governs the "winners" of this competition. As long as trace nutrients and an easily degradable source of organic carbon are available, then it is the availability of terminal electron acceptors and the thermodynamics that leads to a predominance of one biogeochemical process or another. For example, there is more energy to be derived from sulfate reduction than methanogenesis, so as long as there is sulfate present, sulfate reducers will out-compete methanogens. This simple explanation of bacterial competition is often complicated in nature by the capacity of methanogenic bacteria-produced methane to diffuse away from its original point of production (Borowski et al. 1996). Should that methane diffuse into zones where bacterial sulfate reduction is taking place, then the biogenic methane itself can become the preferred organic carbon source for the sulfate reducing consortia and will be oxidized to bicarbonate (Borowski et al., 1996). For this study, methane was used as a carbon source simply for computational efficiencies in the thermodynamic modeling and not meant to imply that methanogenesis plays any potential biogeochemical role in this sulfate-rich setting.

This biological process was evaluated using the USGS geochemical reaction path model, PHREEQC. The model provided theoretical support for the possibility of biogenic sulfate reduction as a solution at this site and possibly at many other similar sites. In the model, methane was chosen as the organic carbon source because it is the most reduced form of carbon with thermodynamic data available in the model. The progression of sulfate reduction is shown by the increase in partial pressure of this reducing species. The model results show that the water can be remediated to near or within drinking water standards for most constituents.

Some of the positive environmental effects related to biogenic sulfate reduction include the increase of pH and alkalinity and the overall decrease in TDS. The pH increases due to the consumption of protons during reduction of  $\text{SO}_4$  to  $\text{H}_2\text{S}$  (Figure 3). The alkalinity (e.g. dissolved bicarbonate,  $\text{HCO}_3^-$ ) steadily increases as the environment becomes more reducing because bicarbonate is produced during the coupled reduction of sulfate and oxidation of organic carbon. There is an overall decrease in the TDS as the contaminants precipitate out as their relatively insoluble oxide and sulfide phases.

The remediation effort can be measured in the decreased concentration of contaminating species. Model results suggest that the aqueous iron is completely removed from solution by  $\log P_{\text{CH}_4} = -11$  as it precipitates as pyrite which is determined from change of moles in solution in model output. (Figure 3). The concentration of  $\text{H}_2\text{S}$  in the system has an inverse relationship with the concentration of sulfate as it is converted into hydrogen sulfide. Most of the calcium is also removed from solution late in the process as the precipitation of calcite begins. The removal of As, U, and Fe are the most significant. This effect is vital to this site due to the high concentrations of uranium present. Saunders et al. (1997b) suggested that although the model shows precipitation of arsenic in the form of orpiment ( $\text{As}_2\text{S}_3$ ), in actuality it most likely will coprecipitate in  $\text{FeS}$ .

The amount of sulfate removed by this process relies on many interdependent factors. The model results suggest that most of the sulfate can be removed but not necessarily enough to bring the water to within the drinking water standards for sulfate. The amount removed will be a function of the number of bacteria and amount of contaminants present to stimulate the bacterial metabolism. Some limiting conditions, such as amount of organic carbon, will also affect the process, and until a field test is completed the impact of each effect can not be quantified.

Recently we have proven that indigenous SRB can be stimulated by this technique at another site where groundwater is contaminated by sulfuric acid and six heavy metals including Pb and Cd (Saunders, unpublished data). The groundwater around the injection well at this site, an automobile and airplane battery recycling plant in Alabama, was successfully remediated to well below the drinking water standards for the contaminating metals, and the pH increased one log unit. However, there are still some questions and practical concerns about the field application of this technology. There are two possibilities for adding the carbon into the subsurface. These methods are injection through the wells and sprinkling of carbon compounds at the surface, however the most effective way may be a procedure that combines both methods (Saunders,

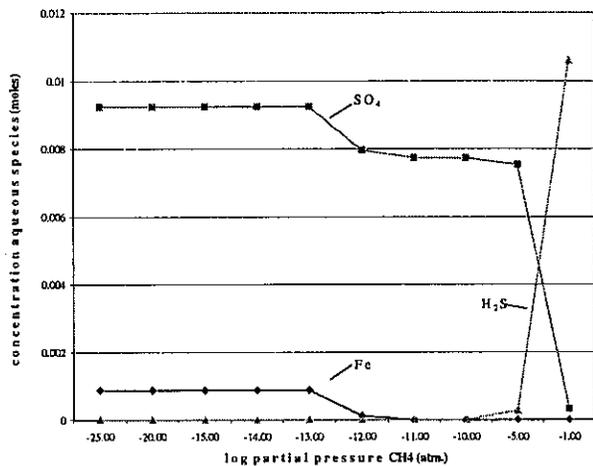


Figure 3. Plot of model results of aqueous species concentrations vs. log partial pressure of methane. The decreasing concentration of SO<sub>4</sub> mirrors the increase in H<sub>2</sub>S during the reduction process. The Fe concentration decline is due to precipitation of pyrite.

1998). The technology may be most successful if a geochemical barrier is set up at the edge of the plume by installing a fence of injection wells. This outer fence of wells, essentially a "permeable reactive barrier" developed from injection of nutrients through the wells, would provide a final opportunity to further remediate groundwater already treated in the contaminated plume.

As previously discussed, H<sub>2</sub>S is produced during the bioremediation process. Presently field tests have not shown whether there will be any toxicity effects on the bacteria or the concentration of H<sub>2</sub>S at which these effects will begin. H<sub>2</sub>S is known to be toxic to SRB, however this toxicity may be an indirect effect since H<sub>2</sub>S will remove ferrous iron as it precipitates as pyrite, thus denying the bacteria the required ferrous iron for their metabolism. Another possible problem is biofouling, which could cause clogging of the aquifer with biomass or mineral precipitates. Another valid question is whether the system will remain reducing as the water table fluctuates or as the organic carbon source is depleted. These questions must be evaluated in our large-scale field test that scheduled to begin in 2000.

### Conclusions

The prevailing geochemical and geomicrobiological conditions at the site indicate that indigenous sulfate-reducing bacteria can be stimulated by the addition of water-soluble organic carbon to

effect in situ bioremediation of contaminated groundwater. Proof of this concept has been demonstrated at another similar site (e.g., high levels of dissolved sulfate, acidic conditions) not related to phosphate mining. The technique should prove to be much more cost effective than currently available technologies, if the process can be optimized for full-scale use. However, potential limitations (e.g., long-term aspects) of the technology await further research. A field test at the site is planned in the near future.

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