

TREATMENT OF BERKELEY PITLAKE WATER USING THE GREEN PRECIPITATE PROCESS

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ABSTRACT

Acid mine drainage (AMD) is usually treated by air oxidation followed by addition of lime to precipitate metal hydroxides and calcium sulfate. Geo2 Limited of Melbourne, Australia, has developed and patented a novel alternative precipitation scheme based on the formation of mixed valency, M(II)-M(III), hydroxide sulfate salts. When the composition of AMD has an appropriate ratio of Fe(II):Fe(III), the green precipitate process provides a useful and more effective alternative to conventional liming. Many acidic mine drainage waters consist predominantly of Fe(II), particularly near their source, and it is these where the green precipitate (GP) process can be used with most positive effect. The GP process incorporates a pipe reactor to prevent or control oxidation.

The characteristics of the precipitate and utility of the green precipitate process are described here in terms of underlying chemistry and innovative process equipment. Demonstrations in the United States where Berkeley Pitlake water was treated are described. A mobile, pilot pipe reactor rig was built to demonstrate the process and was used successfully in these trials in Butte, Montana.

Key words: acid mine drainage, green precipitate process

INTRODUCTION

In conventional liming processes where the iron in AMD is mostly Fe(III), the “ferric hydroxide” precipitate is either *ferrihydrate* or *schwertmannite*, and the material is poorly crystalline, slow to settle and difficult to filter. In that situation the neutralization procedure is often preceded by aeration to oxidize Fe(II) to Fe(III), which can be a very slow reaction which adds significantly to overall costs.

The GP process involves the formation of an Fe(II)-Fe(III) hydroxide sulfate hydrate compound with the general formula $\text{Fe}^{\text{II}}_x \text{Fe}^{\text{III}}_y (\text{OH})_{2x+3y-2z} (\text{SO}_4)_z \cdot n\text{H}_2\text{O}$, which is a green-colored precipitate in which either the bivalent or the trivalent iron can be replaced by other bivalent or trivalent metal ions. Many other divalent metals will incorporate into the precipitate structure, and Al(III) which is common in AMD, will substitute as a trivalent metal. It is also possible to have substituting anions such as carbonate and chloride. The compounds that are formed are said to belong structurally to the *pyroaurite-sjögrenite* group of hydroxides with the essentially Fe(II) trioctahedral structured iron hydroxide layers carrying a positive charge, alternating with layers consisting of anions and water. In AMD a significant amount of the predominant sulfate anion is removed from solution in the green precipitate, together with various forms of calcium sulfate when lime has been used as the neutralizing reagent.

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aeration to oxidize Fe(II) to Fe(III) and this can be a very slow reaction which adds significantly to overall costs. Also in conventional liming processes there are problems in the preparation of lime slurry where carbonation from atmospheric CO₂ will lead to the formation of calcium carbonate scale. The GP process as exemplified in using the coiled pipe reactor pilot plant incorporates an auxiliary reactor in which the lime is premixed and introduced into the pipe reactor in the absence of atmospheric air, either at the inlet of the reactor or at multiple points along the pipe.

Many acidic mine drainage waters consist predominantly of Fe(II), particularly near their source, and it is these where the GP process can be used with most positive effect. Where the requirement of AMD having significant Fe(II) is met, some further advantages of the GP process are as follows:

- The precipitate will incorporate a wide range of contaminant species, both cation and anion.
- The coarsely flocculent green precipitate with crystalline morphology will settle rapidly, dewater readily, and filter easily.
- The lime requirement is less than for conventional liming of predominantly Fe(III) drainage waters.
- The process can be effectively performed in a pipe reactor.
- The problem of carbonate formation and scaling in conventional liming processes can be eliminated by utilizing a pipe reactor.
- The removal of sulfate in the GP compound is of benefit.
- Metal values such as Cu and Zn can be leached directly from the green precipitate by a selective leach process, and then easily recovered.

Green-colored precipitates based on the mixed valency Fe(II)-Fe(III)-H₂O system have been known for many years. Most studies of the green compounds concentrated on the formation and properties of Fe(II)-Fe(III) hydroxides which became known as “green rust” (GR), because of their color and formation when iron corrodes in the presence of oxygen. In early work the compounds were referred to as ferrosic hydroxide, ferroso ferric hydroxide, or basic ferrous ferrite, and given the formula Fe₃(OH)₈ which dates back to the work of Deiss and Schikorr (1928), and Girard and Chaudron (1935). A “solubility product” for Fe₃(OH)₈ was proposed by Arden (1950), at which time Feitknecht and Keller (1950) also reported the dark green compounds containing iron in their two oxidation states. Bernal, Dasgupta, and Mackay (1959) first attempted to elucidate structure, and structural studies have been continuing over many years (Allman, 1970; McGill et al., 1976; Murad and Taylor, 1984; Kanzaki and Katsura, 1986; Cuttler et al., 1990; Génin et al., 1996). There have also been studies of those compounds where there has been replacement of either the divalent or trivalent iron with other cations, and also where there has been incorporation of anions into the interlayer (Stampfl, 1969; Taylor, 1973; Brindley and Bish, 1976; Taylor and McKenzie, 1980; Taylor, 1980, 1984; Taylor et al., 1985; Hansen, 1989; Taylor et al., 1991; Drissi et al., 1995). The anions carbonate and sulfate have been given particular attention.

Other important contributions to a basic understanding of the formation of GR compounds have been made by a number of soil scientists who have proposed that these compounds take part in the chemical reactions that occur in anoxic soils (Ponnampetuma et al., 1967; Collins and Buol, 1970; Schwab and Lindsay, 1983; Van Breemen, 1988; Schwertmann and Fechter, 1994; Trolard et al., 1996, 1997). It was the senior author of this paper, a soil scientist, R. M. Taylor, who first suggested that the formation of these mixed valency Fe(II)-Fe(III) hydroxide sulfates were important in the geochemical scene.

The studies, mostly by corrosion scientists and soil scientists, of the mixed valency Fe(II)-Fe(III) hydroxide compounds have led to the term “green rust” or simply GR. When carbonate is incorporated into the structure, the material has been called “carbonate green rust” or “green rust 1” or simply GR1(CO₃²⁻), and Mössbauer studies and stoichiometric analysis has led to the general acceptance of an Fe(II):Fe(III) ratio of 2:1 in this compound and a chemical formula of (Fe^{II}₄Fe^{III}₂(OH)₁₂)(CO₃·2H₂O). In the case of “sulfate green rust” or “green rust 2,” the term is GR2(SO₄²⁻) and it has an approximate composition (Hansen et al., 1994) of [Fe^{II}₄Fe^{III}₂(OH)₁₂][SO₄·3H₂O]. Trolard et al. (1996) have proposed that as a mineral it be called *fougérite*. The work conducted by the senior author of this paper indicates that there is a degree of variation in the Fe(II):Fe(III):SO₄ ratio in the green precipitates.

THERMOCHEMICAL EVALUATION OF GR2(SO₄²⁻)

The chemistry and stability of GR2(SO₄²⁻) can be best explained in terms of E_H and pH, and shown on a potential pH diagram. Possibly the first paper to show the stability region for the green precipitate on E_H-pH diagrams was published by Biernat and Robins (1972) who used the formula xFe(II).yFe(III).O_y(OH)_{2x+y} for the compound. A stability region for GR2(SO₄²⁻) was shown on E_H-pH diagrams published by Detournay et al. (1975), and in more recent literature Génin et al. (1996) have re-evaluated data and produced a similar diagram for the GR2(SO₄²⁻) system. Potential pH diagrams for carbonate green rust (Drissi et al., 1995) and chloride green rust (Refait and Génin, 1993) also appear in published literature. Free energies of formation for GR2(SO₄²⁻) were used in the papers by Detournay et al., (1975) and Génin et al. (1996) for their potential pH diagrams, and a revised value obtained by Hansen et al. (1994) from the experiments described in their paper.

Revised potential-pH diagrams for the Fe(II)-Fe(III)-SO₄²⁻-H₂O system have been constructed by the authors of this paper to better understand the conditions and reactions which are involved in the Geo2 GP process. The calculations involved the use of free energy data which are consistent with CODATA Key Values for Thermodynamics (Parker and Khodakovskii, 1995), extended by using critically selected data from the CRITICAL Data Base (NIST, 1995), as in Table 1, and used in a computer program which minimizes free energy and plots the required diagram. For

these calculations it was also necessary to obtain free energies of formation for the $\text{GR2}(\text{SO}_4^{2-})$ compound itself, which we will call green precipitate and use the formula $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4$ or $\text{Fe}_6(\text{OH})_{12}\text{SO}_4$ without specifying the degree of hydration, and for the compound which first precipitates in the green precipitate process, for which we give the formula $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ (again without specifying the degree of hydration). To do this we have used a titration method similar to that of Hansen et al., but where a number of different solutions containing various levels of sulfate and total iron ($\text{FeII}:\text{FeIII}\sim 2$) were titrated with sodium hydroxide. A typical titration result is reconstructed in Figure 2. These titrations were the basis for the calculation of the free energies of formation for both $\text{Fe}_6(\text{OH})_{12}\text{SO}_4$ and $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$, which were used for the computation of EH-pH diagrams such as the one in Figure 1 (This diagram in Figure 1 is in fact a simplified and modified composite diagram to illustrate the course of reaction in the GP process.). In order to model the green precipitate process and predict the conditions that will apply at different concentrations, the free energies of all appropriate species likely to be involved need to be used. Table 1 shows the free energy data that have been used by the authors for that purpose. The details of the calculations used to convert titration data to free energies and for the production of stability diagrams are outside of the scope of this paper.

In the titration experiment, a yellow precipitate forms at first at about $\text{pH}=3$; the pH then rises to about 6 when the precipitate becomes green and remains that color to higher pH levels. The course of these changes is shown by the arrows on the potential-pH diagram in Figure 1, essentially identifying the chemical stability basis of the green precipitate process. Most commonly, lime is used as the alkali in the GP process, and this results in the precipitation of *gypsum*, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, mostly in the initial stages of precipitation, finally to give a mixture of *gypsum* and green precipitate.

The change from $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ to $\text{Fe}_6(\text{OH})_{12}\text{SO}_4$ in the green precipitate process is slow as it entails a solid-state reaction which may take several minutes for completion. The whole process also needs oxygen-free conditions to prevent the oxidation of Fe(II) to Fe(III). These requirements led Geo2 to develop a continuous-flow pipe reactor for the process.

VARIATIONS IN THE GREEN PRECIPITATE PROCESS

Geo2 has adapted the green precipitate process to a variety of AMD problems and in doing so has used several alkaline reagents for controlling pH. These have included lime, limestone, precipitated calcium carbonate, and alkaline process tailings.

The most common alkali reagent for AMD control is lime, $\text{Ca}(\text{OH})_2$, but in its conventional use there is the problem of carbonation from air contact and the resultant scaling of process pipes and vessels. The calcium carbonate formed by air carbonation is often very hydrophobic and will tend to float and overflow settling tanks and thickeners. Geo2 has developed a lime-mixing vessel which does not allow air contact, and will feed a controlled composition lime slurry directly into a pipe

reactor which will then not suffer from scaling problems. This precaution against carbonation can result in a carbonate-free green precipitate which can be an advantage in some cases. In the GP process, when lime is used, it is not added in excess and the final pH can be lower than that at which CaCO_3 can form when the end slurry is contacted with air.

When lime, limestone, or calcium carbonate are used to neutralise AMD, another insoluble product is calcium sulfate which usually supersaturates the solution and leaves the filtered or settled clear water high in calcium and sulfate. In the GP process, several techniques of seeding and otherwise nucleating the supersaturated solution have been used successfully, and bubbling CO_2 through the solution will further reduce calcium levels.

After precipitation of the green precipitate, it can be selectively leached to recover certain metal values. Geo2 has utilized a leachant which removes Cu and Zn from the GP, and this leaching procedure was performed in the 1997 BPIT demonstration in Butte, Montana, where Zn and Cu recoveries better than 80% were demonstrated.

Another variation in the GP process is to use a method of controlled oxidation to convert the green compound to a phase which can be recovered by virtue of its magnetic properties.

The process was developed by Geo2 in Australia, initially in a bench scale 400 mL glass titrator apparatus which was closed to the atmosphere, had gas ports and atmosphere control facilities, and was fitted with a pump for introducing alkali at a rate controlled by a predetermined pH regime. The chemistry and kinetics for the neutralization and metal ion removal from a number of AMD waters was investigated, and the characteristics of the green precipitate were studied, modified with various reagents, and converted to other compounds.

In Australia, water samples from the Berkeley Pit in Butte, Montana, were treated in the Geo2 batch reactor, giving excellent removal of metals and a precipitate which could be dewatered very easily. In comparison with the normal lime precipitation of oxidized water, the GP process was superior in every way. In 1996, Geo2 was invited to perform bench-scale demonstrations on Berkeley Pit water in Butte under the Berkeley Pit Innovative Technologies program supported by the U.S. EPA and the U.S. DOE as a part of an interagency agreement on mine waste technologies. Again in 1997, Geo2 was invited to demonstrate Cu and Zn recovery from the precipitate formed in a 30 L bench-scale reactor for the green precipitate process, and also took to the U.S. a larger pilot-scale coiled pipe reactor and provided demonstrations to a wider audience. Some of the results from applying the GP process to Berkeley Pit water are shown in the following section.

EXPERIMENTS WITH BERKELEY PIT WATER

For over 100 years the "Butte Hill" has been mined extensively for copper and other metals. The mining was confined to underground operations from about 1876 to 1975 when the vein mining was discontinued. In 1955, an open-pit mine (the Berkeley Pit) was commenced and mining contin-

ued there until 1982. The groundwater infiltrating both the Berkeley Pit and the old underground workings was pumped at a rate of about 5,000 Gpm before mining ceased in 1982. Since pumping was stopped in that year, the water table has been recovering and the pit and associated underground mines have been filling with water. Initially in 1982 the water level rose over 1,300 ft in the underground workings, and in recent years has been rising about 25 ft per year in the Berkeley Pit. In 1996, the rise in water level was continuing at a rate of about 16 ft per year above a water depth of about 900 ft. It is considered that there may be potential for the water level to rise to an elevation where the hydraulic gradient reverses and the pit water migrates into both groundwater and surface water systems. Many process options have been demonstrated for remediation of this pit water.

The water in the pit has been sampled and analyzed at regular intervals since 1984 and good accounts of the geochemistry of the system have been published. This water is extremely well characterized and recognized as a standard material for use to demonstrate remediation technologies. The water is acidic (pH~2.7) and contains elevated concentrations of metal ions, sulphate, and arsenic. The Fe(II):Fe(III) ratio increases with depth and Geo2 believes that pumping water from depth and feeding it to an appropriate green precipitate reactor would be a more effective remediation process than the conventional aeration-lime neutralization procedure.

BENCH SCALE EXPERIMENTS IN A 400 mL GLASS APPARATUS

These were performed in Butte, Montana, in August 1996 and are reported in detail in a Final Report (1997). The work was strictly controlled by the QA/QC procedures that are required by U.S. EPA. Briefly, samples of Berkeley Pit water taken from a depth of 200 feet were treated in a 400 mL titrator with inert atmosphere and subjected to controlled addition of various alkaline reagents. Analyses of the original pit water and the water at the end of the different experiments are shown in Table 2. The full details of treatment are not given here but are contained in the Final Report on the demonstration.

BENCH-SCALE EXPERIMENTS IN A 30 L LABORATORY REACTOR

In August 1997, Geo 2 was again selected as part of the BPIT program to demonstrate the green precipitate process in Butte, Montana. On this occasion, a 30 L laboratory reactor was used for the demonstration which was primarily concerned with the recovery of metal values from the precipitate. Selective leaching of copper and zinc was demonstrated in experiments where >90% of the Cu and >88% of the Zn were recovered. The experiments were considered to be very successful and have been documented in a Final Report on the work.

PILOT-SCALE DEMONSTRATION IN THE MOBILE COILED PIPE REACTOR

A mobile, pilot-scale coiled pipe reactor rig was built in a 2m x 2m x 5m frame for truck or ship transport so that on-site trials and demonstrations could be conducted at close proximity to an

AMD source. A photograph of the rig is shown here as Figure 3. The pipe is 25 mm diameter plastic, wound in layers of 50 meter lengths, with by-pass valving to enable a variety of residence times. The maximum length is 600 meters. Clear plastic sections allow flow observations and multi-point instrument electrode ports for pH or E_H probes are provided. There is provision for introducing lime slurry, flocculant, or other reagent at multiple points along the pipe, with precision metering pumps through mixing devices that will not allow air contact and will control particle size with oversize reject. A stirred-bead mill can be used for fine milling of lime or other reagent. There are programmable logic controls for automation of monitoring and control.

The system will operate at flow rates between 10-100 liters per minute, and the residence time can be controlled to attain full development of the desired green precipitate characteristics.

The main advantages of a pipe reactor system for the Geo2 green precipitate process are as follows:

- Exclusion of air from the system maintains an appropriate Fe(II)/Fe(III).
- All material in the system is subject to a uniform residence time which can be easily controlled by flow adjustment.
- Monitoring the system with in-line detectors (E_H , pH etc.) is easily accomplished, and facilitates control.
- Dosing of the system at different points in the reaction with various reagents such as alkali or flocculant is possible.
- Construction of the system as a coiled pipe is economical, but other orientation could provide advantage in terms of materials transport.

PROBLEMS ASSOCIATED WITH THE USE OF LIME IN TREATING ACID EFFLUENTS

When lime, $\text{Ca}(\text{OH})_2$, is slurried in water to the point of saturation, a pH of about 12.4 will be reached and about 940 mg/Litre of $\text{Ca}(\text{OH})_2$ will go into solution ($\log(\text{Ca}^{2+}) = -1.9$). This slurry, if agitated in contact with air, and particularly if air is sparged through the mixture or even when a vortex is formed in the surface of a stirred tank, will react with the carbon dioxide in the air (P_{CO_2} in air is $10^{-3.47}$ atmospheres or about .034% by volume.). This reaction can be very fast depending on the slurry density and the rate of air contact, and can result in the conversion of calcium hydroxide to calcium carbonate within a period of 24 hours. The pH of the solution when the calcium hydroxide is finally all converted to calcium carbonate will fall to about 8.3 with $\log(\text{Ca}^{2+}) = -3.3$.

During this process, the calcium carbonate will form a scale on surfaces and cause problems of blockages in pipes and other equipment. So in mixing lime, it could be advisable to avoid contacting the slurry with air.

Also when lime is used in neutralising acid solutions to say pH=12 and the resulting slurry allowed to settle, in a thickener for example, the carbonation reaction will continue at the still surface. In this case, calcium carbonate crystals will form at the surface and will float and overflow

the thickener. In this process it has been recently determined by experiment (L. G. Twidwell, Montana Tech, Butte, Montana) that the rate of CO₂ transfer from the air can be as high as 500 mol CO₂/m²year, which compares with figures of about 10 Mol CO₂/m².year for CO₂ transfer from air to water in normal environments. Obviously the reaction at lime-saturated surfaces is very different and the surface precipitation of a floating calcium carbonate solid not only causes problems but presents an interesting fundamental study.

CONCLUSION

The green precipitate process provides an alternative to conventional liming for the remediation of acid mine drainage which consists predominantly of Fe(II). The new process can be efficiently demonstrated on-site with a mobile, coiled-pipe continuous-reactor rig.

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Table 1. Free energies of formation[§] (p^o=1 bar) for the species which are considered in the iron-sulfur-water system in relation to green precipitate process modeling.

SPECIES	$\Delta G^{\circ}_{29815K}$ kJ/mol	SPECIES	$\Delta G^{\circ}_{29815K}$ kJ/mol
1. H ₂ O (liq)	-237.129	20. FeOH ²⁺ (ao)	-240.93
2. OH ⁻ (ao)	-157.238	21. Fe(OH) ₂ ⁺ (ao)	-464.32
3. Fe ³⁺ (ao)	-16.28 (-4.7)	22. Fe(OH) ₃ (ao)	-359.31
4. Fe ²⁺ (ao)	-90.53 (-78.9)	23. Fe(OH) ₄ ⁻ (ao)	-841.58
5. SO ₄ ²⁻ (ao)	-744.00	24. Fe ₂ (OH) ₂ ⁴⁺ (ao)	-490.53
6. HSO ₄ ⁻ (ao)	-755.36	25. Fe(OH) ₃ (s,am)	-709.46
7. H ₂ S (ao)	-27.89	26. Fe ₄ O ₃ (OH) ₆ (S,4L)	-2126. †
8. Hs ⁻	+12.18	27. FeOOH (s,α)	-488.51
9. S ²⁻	N/A ‡	28. Fe ₂ O ₃ (s)	N/A
10. Fe(HS) ₃ ⁻	-116.71	29. Fe ₃ O ₄ ·nH ₂ O (s)	N/A
11. Fe(HS) ₂ (ao)	-117.26	30. FeOH ⁺ (ao)	-274.03
12. Fe ^{II} SO ₄ (ai)	-834.53	31. Fe(OH) ₂ (ao)	-447.82
13. Fe ^{II} SO ₄ (ao)	-848.17	32. Fe(OH) ₃ ⁻ (ao)	-636.44
14. Fe ^{III} SO ₄ ⁺ (ao)	-783.34	33. Fe(OH) ₄ ²⁻ (ao)	-776.56
15. Fe ^{II} Fe ^{III} (SO ₄) ₂ ⁺ (ao)	-1618.??	34. Fe(OH) ₂ (s,am)	-487.37
16. Fe ^{III} (SO ₄) ₂ ⁻ (ao)	-1534.99	35. FeS ₂ (s,pyr)	-160.1 ?
17. Fe ^{III} SO ₄ ·7H ₂ O (s)	-2507.75	36. FeS (s)	-101.3
18. Fe ^{II} ₄ Fe ^{III} ₂ (OH) ₁₂ SO ₄ (s)	-3824.*	37. Fe _{.875} S (s,prh)	-98.9 ?
19. Fe ^{III} ₈ O ₈ (OH) ₆ SO ₄ (s)	-4095.*	38. Fe _{.9} S (s,prh)	-99.6 ?

§The data are mostly consistent with CODATA Key Values (Parker and Khodakovskii, 1995) and the CRITICAL Database (NIST, 1995). Data for Fe²⁺ and Fe³⁺ in this table are compared to those in The NBS Tables (D. D. Wagman *et al.*, 1982)

‡For discussion see Inorg. Chem., 22 (1983) 2345-2346. (pKa2 ~ 17)

*These values are conditional free energies of formation, $\Delta G^{\circ}_{298.15 K}$ kJ/mol, and assume that the compound is in fact hydrated and that the free energy of one mole of the water of hydration is equal to that for one mole of liquid water. The free energy for Fe^{II}₄Fe^{III}₂(OH)₁₂SO₄(s) was calculated initially from the results of the work of Hansen *et al.*, 1994.

†A conditional Free Energy of Formation for 4-line *ferrihydrite*, expressed as Fe₄O₃(OH)₆, which is consistent with CODATA Key Values.

?These data from USGS Bull. 2131 (1995) are not consistent with CODATA Key Values (1995).

Table 2. Analysis of Berkeley pit water before and after treatment.

Sample	As ppm	Se ppb	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO ₄ gpL	pH SU
B. Pit Water	BDL	1	288	209	1070	BDL	572	189	1.96	9.5-10.6	2.9
MT1	BDL	BDL	1.325	6.36	0.112	BDL	0.087	BDL	BDL	3.375	8.0
MT2	BDL	BDL	0.11	5.1	BDL	BDL	BDL	BDL	BDL	3.0	7.9
MT3	BDL	BDL	1.25	5.14	BDL	BDL	BDL	BDL	BDL	3.25	8.0
MT4	BDL	1	0.375	0.125	0.125	BDL	BDL	BDL	BDL	7.5	8.6
MT5	BDL	1	BDL	1.74	BDL	BDL	0.075	BDL	BDL	7.75	8.8
MT6	BDL	2	0.25	17.25	BDL	BDL	.1625	BDL	BDL	8.125	8.1
MT1A	BDL	BDL	1.35	6.46	0.112	BDL	0.212	BDL	BDL	4.0	5.9
MT2A	BDL	BDL	1.25	5.0	BDL	BDL	0.087	BDL	BDL	3.5	5.6
MT3A	BDL	1	1.025	5.59	BDL	BDL	0.157	BDL	BDL	3.5	5.3

A = Further treatment of gypsum seeding and CO₂ Bubbling

BDL = Below detection limit

Table 3. Some results from the pipe reactor demonstration.

Heavy Metal	Before Remediation (ppm)	After Remediation (ppm)
Aluminum - Al	227	7.44
Arsenic - As	0.058	0.065
Cadmium - Cd	2.247	0.003
Calcium - Ca	437	931
Chromium - Cr	0.230	0.006
Copper - Cr	188	0.0206
Iron - Fe	773	0.001
Manganese - Mn	204	0.135
Nickel - Ni	1.269	0.008
Zinc - Zn	612	0.005

Figure 1. Potential-pH diagram for the Fe-H₂O-sulfate system showing the course of an alkali titration of a solution which initially has a ratio of Fe(II):Fe(III) = 2 at pH = 1. At pH = 2, Fe₈O₈(OH)₆SO₄ commences to precipitate and continues to precipitate up to the incongruent point at pH = 6.3 where the Fe₈O₈(OH)₆SO₄ then converts to Fe₆(OH)₁₂SO₄ (the green precipitate).

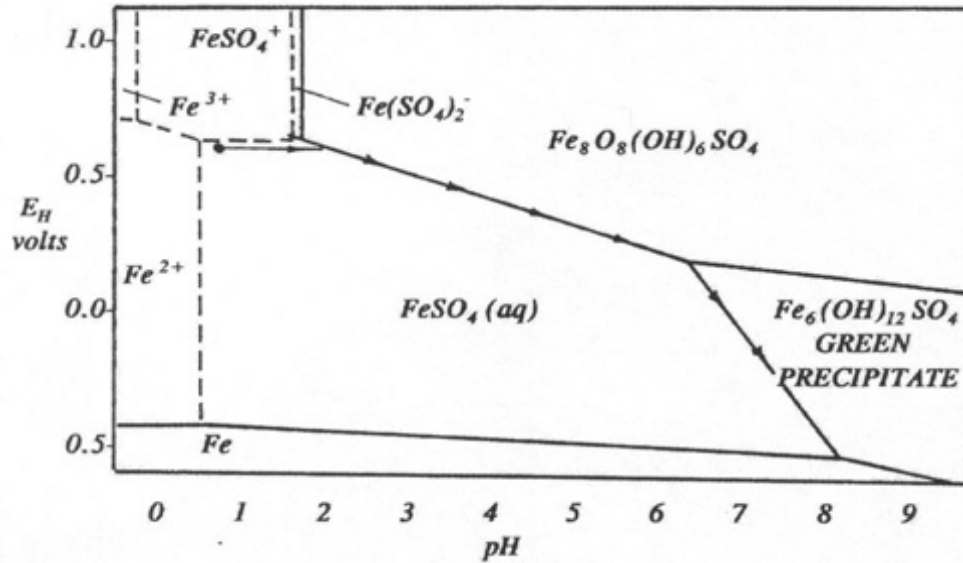


Figure 2. The titration curve, corresponding to the potential-pH diagram in Figure 1, where an Fe(II)-Fe(III) solution has alkali slowly added.

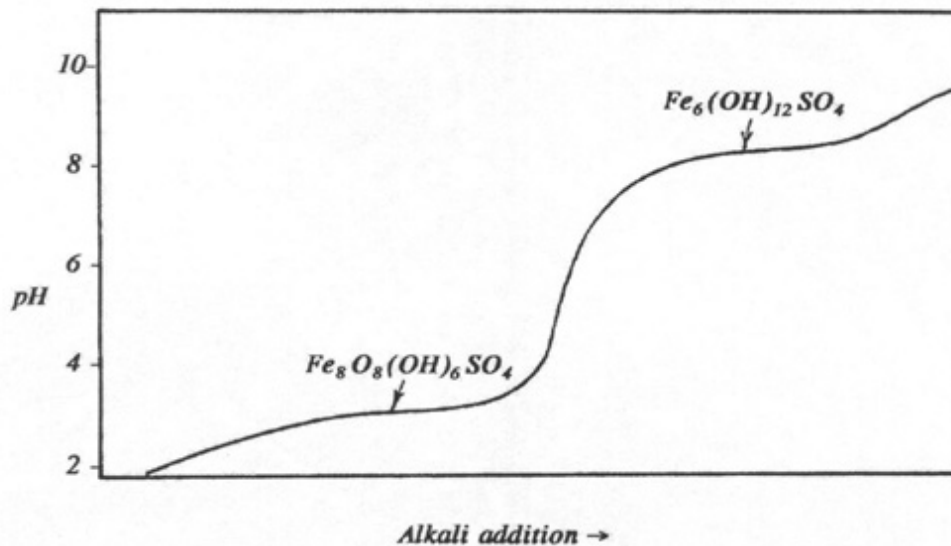


Figure 3. Two views of the Geo2 mobile coiled pipe reactor which is used to demonstrate the green precipitate process on location.

