Active Treatment of High Salinity Mine Water

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Abstract

The treatment of high salinity minewater such as those found in the flooded mine workings underlying the North Sea off the Durham Coast UK offers environmental engineers a unique challenge. Although the water quality is variable, depending on the degree of mixing between the fresh and saline water, it can be characterised as potentially high in iron (up to 100mg/l), chloride (up to 35,000mg/l), sulphate (3,500mg/l) and calcium (2,000mg/l). Due to the high chloride content and net acidity passive treatment is problematic because of the adverse affects of the salinity on plant and microbial growth. The high calcium and sulphate concentrations suggest that active treatment using conventional lime based precipitation could result in significant gypsum precipitation. The treatment of low salinity minewater supersaturated with gypsum at similar concentrations has resulted in the build up of scale on the process equipment and produced a sludge containing significant quantities of gypsum.

Therefore when faced with a request from the UK Coal Authority to install an active treatment system at the former Horden Colliery site in County Durham, IMC Group Consulting Ltd (IMC) and process solution provider Unipure Europe Ltd (UEL) were concerned with the affects of gypsum precipitation on the mass (and volume) of sludge produced and the risk of scale building up in the reaction vessels, pipes, etc. To establish the potential implications of gypsum precipitation IMC and UEL employed a combination of theoretical analysis and laboratory pilot plant trial techniques to provide design data for the process plant.

As a simple stoichiometric assessment based solely on the solubility of calcium sulphate, revealed that some 4.9gm/l of gypsum would be pre-

cipitated. A more detailed assessment was undertaken using PHREEQC. This revealed that although the minewater is theoretically supersaturated in gypsum, the high chloride concentrations reduced the activity of the calcium sufficiently to limit gypsum precipitation.

To confirm this prediction and provide process design data, UEL in conjunction with Cardiff University undertook a series of laboratory scale pilot plant trials using a synthetic minewater solution made from seawater dosed with iron (Iron II chloride) and calcium chloride. The results from the trials demonstrated that despite the relatively high calcium and sulphate concentrations the resultant sludge only contained approximately 1% sulphate.

This paper discusses the results from the PHREEQC modelling and pilot studies in terms of predicting the mass of gypsum precipitated form high salinity mine water.

Introduction

As a result of rising groundwater levels along the coast to the east of Durham, The Coal Authority has installed a temporary minewater treatment plant (TMWTP) at the site of the former Horden Colliery. The plant pumps and treats up to 540m^3/hr (150l/s) from the capped mine shaft to stabilise groundwater levels, thereby prevent saline mine water polluting the locally important Permian Sandstone Aquifer.

Unipure Europe Ltd was appointed by the Coal Authority in Aug 2003 to design and build a temporary mine water treatment plant. Because of the anticipated high salinity of the water it was decided to undertake a series of laboratory trials at Cardiff University to simulate treatment of the mine water. Data from these trials formed the design basis for the plant currently operating at Horden.

The design of the TMWTP was based around the high density sludge (HDS) process. The HDS process was developed in the 1960's (Kostenbader et al, 1970) to counter the problem of high sludge volume problems associated with conventional hydroxide precipitation. By using recirculated sludge to encourage particle growth, rather than the formation of new hydroxide particles, the volume of sludge produced can be minimised (See Coulton et al 2003b).

Sampling revealed a stratified water column within the shaft, with fresh water near surface and highly saline water at depth. To reduce the risk of disturbing this stratification, IMC developed a pumping strategy which involved pumping from the near surface fresh water. However there was some concern that the required abstraction rate could disturb this stratification and therefore the process was designed to treat water containing high concentrations of chloride, sulphate and calcium (35,000mg/l 3,500mg/l and 2,000mg/l respectively). The calcium and sulphate concentrations in the deep mine water were sufficiently high to suggest that significant quantities of gypsum could be precipitated, resulting in a large amount of sludge and potentially leading to the formation of scale. Therefore a combination of numerical analysis, bench tests and pilot trials were carried out to quantify the amount of gypsum precipitation likely to occur. These involved the following steps being followed:

1. Simple Stoichiometric calculations on worst case water quality
2. PHREEQC modelling on worst case water

3 PHREEQC modelling varying chloride and sodium concentrations
4 Laboratory batch tests varying chloride concentrations
5 Pilot plant trials on worst case water quality.

Simple Stoichiometric Neutralisation Modelling

As part of the conceptual plant design, alkali usage and sludge production rates were calculated using simple stoichiometric modelling based the range of mine water quality parameters summarised in Table 1. These calculations predicted that 0.191 g/l of metal hydroxide would be precipitated along with up to 4.9 g/l of calcium sulphate. On this basis only 3.7% of the sludge mass produced by the plant would be iron hydroxide.

Table 1 Assumed Influent Water Quality Range

Parameter	**Range**
pH	5 to 7
Chloride concentration	Up to 35,000mg/l
Sulphate concentration	Up to 3,500mg/l
Dissolve Iron	Up to 100mg/l
Calcium	Up to 2000mg/l

PHREEQC modelling

Because the stoichiometric analysis indicated a significant risk of gypsum formation, PHREEQC was used to provide a more robust assessment of the risk of gypsum formation over the anticipated range of chloride concentrations. The general water chemistry summarised in Table 2 was maintained constant whilst the chloride concentration was varied between 5,500mg/l and 35,500mg/l. The sodium concentration was also varied to maintain the overall charge balance.

The results from the PHREEQC analysis are summarised in Table 3 and reveal a theoretical reduction in the gypsum saturation index with increasing chloride concentration. In particular the results indicate that significant gypsum precipitation is unlikely to occur until the chloride concentration dropped to less than about 20,000mg/l.

Table 2 General Chemical Conditions used for PHREEQC Modelling

Variable	Value
Temperature (°C)	17.5
pH	5.9
Alkalinity (mg/L as $CaCO_3$)	17
Ca (mg/L)	1,630
Mg (mg/L)	1,020
Na (mg/L)	21,822
K (mg/L)	2,020
Fe (mg/L)	27.1
Al (mg/L)	0.37
Mn (mg/L)	2.06
S (6) (mg/L)	3,860
Cl (mg/L)	35,500
N (-3) (mg/L)	6.8
CO_2 (g)	$10^{-3.5}$
O_2 (g)	$10^{-0.67}$
Caustic soda (mole L^{-1})	0.0017

Table 3 Saturation indices for gypsum for decreasing theoretical chloride concentrations in Horden mine water

	Solution conditions			
Chloride concentration (mg/L)	35,500	25,500	15,500	5,500
Sodium concentration (mg/L)	21,822	15,344	8,866	2,388
Gypsum saturation index	**-0.02**	**0.03**	**0.11**	**0.24**

Batch Tests

A series of batch trials were undertaken at Cardiff University to confirm the results for the PHREEQC modelling using synthetic effluent waters created from mains tap water with the chemical composition shown in Table 4.

Table 4: Batch Trials- synthetic Mine Water Chemistry

Chemical	Concentration	
Sulphuric Acid	0.25mg/l	
Iron II Sulphate	100mg/l	Fe
Sodium Sulphate	3,500mg/l	SO_4
Calcium Chloride	2,000mg/l	Ca

The concentration of chloride in solution was increased by the addition of sodium chloride to give concentrations of 5,000 to 35,000 mg/l chloride in 5,000 mg/l increments.

A 1litre sample was tested in each test by adjusting the pH with the addition of a 10% NaoH solution to the target value of 8.5. This was held for a period of 30 minutes whilst concurrently vigorously mixing and aerating the sample. On completion of the test the solids were allowed to settle and were recovered and dried prior to analysis.

The results to the batch trials are presented in Table 5 and displayed in Figure 1.

Table 5 Batch Test Results

Target Chloride Conc. (mg/l)	Final pH	Vol of 10% NaOH added	Measured chloride concentration (mg/l)	Mass of solids (g)	Iron % of Solids	Calcium % of Solids	Sulphate % of Solids
3,545	8.47	9	4,000	6.92	1.44	11.55	48.69
5,000	8.50	9	6,000	6.46	2.20	13.87	45.02
10,000	8.46	8	11,500	5.12	2.12	11.78	38.96
15,000	8.46	9	20,000	4.59	3.66	8.73	29.38
20,000	8.56	8	25,000	14.80	2.33	9.71	27.92
25,000	8.50	8	30,000	7.40	1.97	11.53	30.98
30,000	8.53	8	35,000	7.75	1.98	4.74	35.67
35,000	8.50	8	40,000	6.05	1.24	9.28	9.96

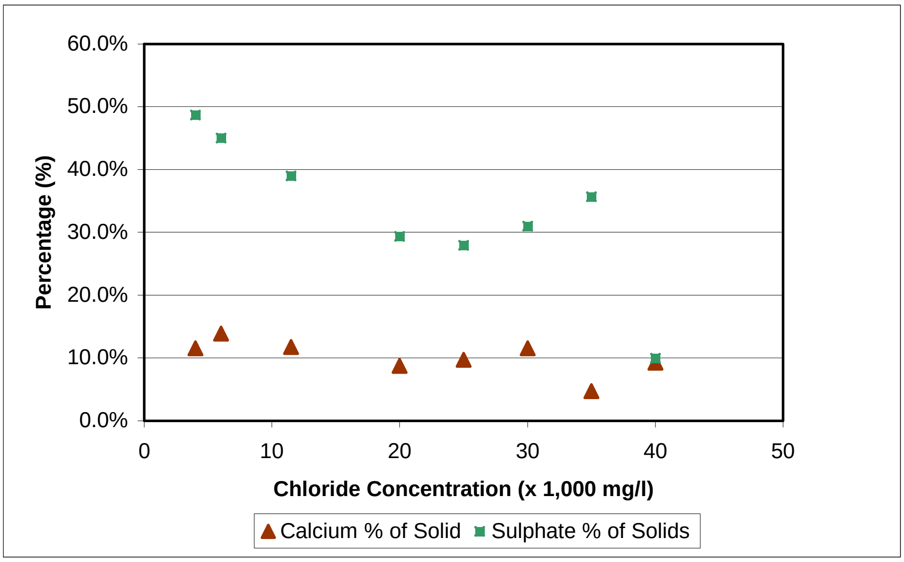

Figure 1 Batch Test Variation in Sludge Calcium and Sulphate concentration

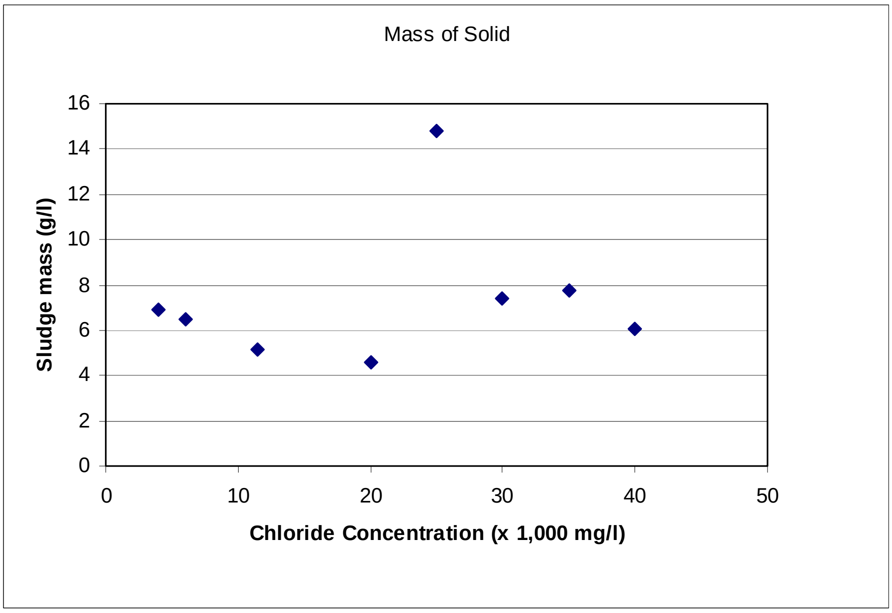

Figure 2 Batch Trial Variation in Sludge Mass Generated

Figure 1 indicates a general decline in the sludge sulphate concentration with increasing chloride concentration, with the exception of the results for chloride concentrations of 30,000 and 35,000mg/l. Figure 2 shows little variation in the mass of sludge generated except for the 25,000mg/l test which generated twice the sludge mass. Visual examination of the dried sludge samples revealed that:

- The lightest coloured sample was obtained from the 4,000 mg/l chloride concentration test. This had the highest sulphate content.
- The darkest sample was obtained from the 40,000mg/l chloride concentration test. This had the lowest sulphate content.
- The sludge from the 30,000 and 35,000mg/l chloride tests did not follow this trend as both samples displayed a light colour.

Pilot Plant Trials

To confirm the design parameters for the Horden plant whilst treating highly saline mine water, pilot plant trials were undertaken using a synthetic solution comprising of seawater containing 100mg/l of dissolved iron, 2,000 mg/l of dissolved calcium, and 3,500 mg/l of sulphate.

The plant layout is shown schematically in Figure 3 and comprised;

- An influent water storage tank and feed pump
- Feed mixing chamber
- Stage 1 and II reaction vessels
- Flocculation chamber and a clarifier
- Ancillary equipment comprises sodium hydroxide and flocculant make-up, storage and dosing systems and air supply.

The plant was designed to treat a flow of 10l/hr and had 30 minutes retention in both the Stage I and Stage II reactors.

The performance of the pilot plant was assessed by monitoring; water quality, reagent consumption, and sludge settlement characteristics (settling velocity and settled sludge density). Additionally analyses of the recycle sludge samples were also routinely undertaken to confirm the iron and calcium content of the sludge.

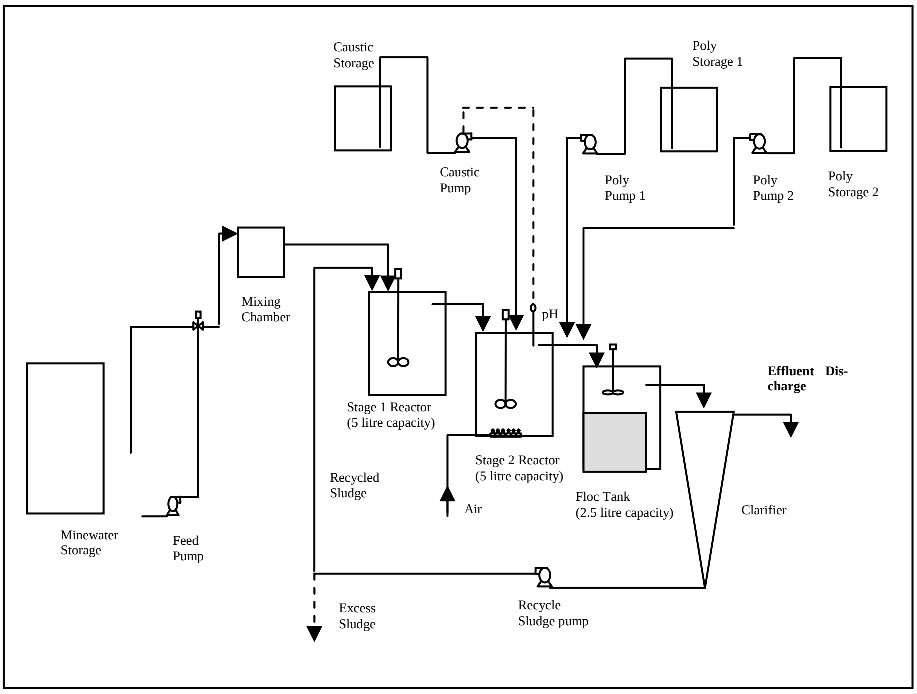

Figure 3 Schematic Diagram of the Pilot Plant.

The pilot trial was run from the 10th Oct 03 to the 1st Nov 03 and during this period the average sludge composition was 31.6% iron, and 11.4% calcium. Analysis of the a sludge sample from the test (Table 6) reveals that despite the high sulphate and calcium concentrations in the feed (2,045 and 2,064mg/l respectively on 12th Oct 2003), the sludge sulphate content was only 1.09%

Table 6 Pilot Plant Final Sludge Composition

Element	Concentration (mg/kg)
Fe	30.7%
Ca	8.48%
SO_4	1.09%
OH	28.6%
CO_3	14.3%

The results from the above analysis indicate that little gypsum precipitation occurred, possibly due to complexing and/or suppression of calcium activity as a result of the high chloride concentration in the seawater.

Conclusions

The results from the predictive analysis and test work undertaken on synthetic samples of saline mine water enabled the Horden Mine Water Treatment Plant to be designed solely on the basis of the amount of hydroxide sludge produced. Demonstrating that gypsum precipitation was not a significant risk had a large impact on the plant design. This allowed a substantial reduction in the size of the sludge recirculation, storage and dewatering systems and resulted in a significant reduction in the plant cost.

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