

# **Application of the PHREEQC geochemical computer model during the design and operation of UK mine water treatment Schemes.**

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## **Abstract**

The number of mine water treatment schemes in the UK has proliferated over the past 10 years, not least through the efforts of the UK Coal Authority, which now operates more than 20 full-scale systems. Significant operating costs associated with these systems include alkali chemical usage (where used), pipe cleaning and maintenance, and sludge disposal. The PHREEQC geochemical model has been used during the design and operation of two of the UK Coal Authority's treatment systems to assess whether it is possible to more accurately predict the fate and behaviour of contaminants through the treatment process, with the ultimate objective of more accurate quantification of alkali requirements and sludge production, and better prediction of treatment system performance.

Two systems have been used for this study, at Frances Colliery, Fife, Scotland, and at Horden Colliery, County Durham, England. The characteristics of the mine waters at these sites, and the treatment systems installed to remediate them, are described. At Frances Colliery the following issues have been investigated using the PHREEQC model:

- Determination of optimum alkali dose rate
- Investigation of secondary mineralization that causes pipe fouling

At Horden Colliery areas investigated using the PHREEQC model are:

- Prediction of sludge volume production for various alkali reagents
- Prediction of the influence of elevated carbon dioxide partial pressures on alkali requirements
- Influence of elevated chloride concentration on sludge characteristics and production

The results of the investigation are presented and discussed. The study suggests that geochemical modelling may be a useful tool in determining both the geochemical processes occurring within a mine water treatment system and ultimately the likely costs involved during the operation of a particular scheme. Plans for future work include further validation of the PHREEQC model predictions by careful sampling and analysis of water chemistry and secondary mineral phases through the treatment systems. In the future it is hoped that the PHREEQC model may become a useful tool in the design phase of mine water treatment systems.

Keywords: Mine water, treatment, PHREEQC model, sludge, alkali, carbon dioxide, chloride

## **1.0 Introduction**

The PHREEQC geochemical model, designed by Parkhurst et al (1995), has been widely used to investigate geochemical processes occurring in aquatic systems. It is capable of simulating a wide range of geochemical reactions including the mixing of waters, addition of net irreversible reactions to solution, and dissolving and precipitating phases to achieve equilibrium with the aqueous phase. The model is able to consider the irreversible dissolution of solid phases under unsaturated conditions. It is also able to use the concept of partial equilibrium to maintain the solutes at saturation with respect to any secondary phases.

The PHREEQC model uses solution ion concentration data that has been recorded onsite, to determine saturation indices for the soluble solution ions. From this information PHREEQC is able to determine the potential for any precipitation of secondary mineral and amorphous phases from within the original solution chemistry under any specified environmental conditions. In order to do this, the model has to balance the chemistry between the secondary, aqueous and gaseous phases taking place by using a series of geochemical reactions.

This paper describes a new application of the PHREEQC geochemical code, namely in the design and operation of mine water treatment systems that incorporate alkali dosing. Since solid phases (i.e. alkali) are required to be dissolved within the PHREEQC model in this application, detailed information regarding the solid phases has to be entered into the model. For the purpose of active mine water treatment, initial information was required by PHREEQC on the three different types of alkali phases that

were available for use in an active mine water treatment system. Any alkali phase not present within the PHREEQC database (e.g. Caustic soda, NaOH) had its solid solution formula entered into the model with a solubility constant selected from published data (Stumm and Morgan, 1996). Atmospheric gases such as carbon dioxide and oxygen were treated as equilibrium phases by the model. Therefore, the model equilibrated the gases with the raw and treated mine water solutions. The model was also able to vary the partial pressures of the gases to simulate the varying gas pressures that the mine water may encounter at depth.

The following study illustrates how the PHREEQC model has successfully been used to make predictions and design decisions at two active mine water treatment systems in the UK. Specific areas that have been investigated are:

- Determination of optimum alkali dose rate
- Prediction of sludge volume production for various alkali reagents
- Prediction of the influence of elevated carbon dioxide partial pressures on alkali requirements
- Influence of elevated chloride concentration on sludge characteristics and production
- Investigation of secondary mineralization that causes pipe fouling

## **2.0 Frances colliery mine water treatment scheme**

### *2.1 Project description*

Mine water recovery in East Fife coal field is currently monitored at eight sites, including the former Frances Colliery Shaft. It was predicted that if no mine water pumping was carried out surface discharge of mine water could occur in 2005. (Recommendations for Mine Water Pumping Levels in the East Fife – IMC, December 2001). Therefore a mine water pumping and treatment scheme was established at the former Frances Colliery site and the first short pump test was carried out in the summer of 2000. (Frances Pump Test – IMC, January 2001). An extension to the treatment area was carried out for the summer of 2002 with pumping recommencing when mine waters reached the proposed trigger level at Frances of 24 m BOD. It is anticipated that mine water levels over all the interconnected mine workings in the East Fife Coalfield may be controlled by pumping at Frances.

The design of the treatment facility at Frances was based on the aim of reducing the total iron in the final discharge to <10 mg/L. i.e. the anticipated consent limit for total iron required by SEPA from any full scheme. Historical information on the nature of the pumped mine water discharged during the previous pump test indicated that the raw mine water could be extremely acidic (1500 mg/L as CaCO<sub>3</sub>, pH 3.5) with significant levels of dissolved iron (up to 650 mg/L). However, it was anticipated that as a result of allowing the level of water in the East of Fife coalfield to rise, the pumped water quality at Frances would improve.

Although, the mine water pumped during the previous pump test was net acid, the possibility that the mine water could be net alkaline was not ruled out. Therefore, the scheme was designed to treat the mine water by simple aeration and settlement techniques using a cascade principle. This method has been well tried and tested on many net alkaline mine waters.

It was decided that in order to ensure that there was sufficient capacity in the proposed settlement facilities it would be appropriate to simply use the maximum pump rates (80 L/sec) and the total iron concentrations of the mine water previously encountered during the last pump test i.e. worst case scenario.

It was known from the previous test that the iron levels in the discharge could be controlled by the addition of caustic soda. Therefore, provision was made in the design for the automatic dosing of 47% caustic soda and flocculent. 47% Caustic soda (NaOH) was added intermittently for the majority of the pump test at a dosage rate varying from 500 L/hour to 640 L/hour for 8 to 9 hours per day. This had the effect of raising the pH of the influent to the settlement ponds to c pH 8.5. The general quality of the mine water during the pump test at Frances Colliery is provided in Table 1.

## *2.2 Determination of optimum alkali dosing rate*

Frances Colliery mine water pumping test was the first scheme where PHREEQC was used to predict the effect of the dosing using the alkali, caustic soda (NaOH) on mine water quality. The geochemical model was used to determine the quantity of caustic soda required to raise the pH from between 6.22 and 6.6 to a target value of 8.5 on a mine water that was passing through the system at 80 l/s. An initial dosing rate of 500 l/hr caustic soda (47%) which equated to 1221 mg/l was input into the model,

as this was the maximum dosage rate available to ensure the mine water discharge remained below the SEPA total iron consent concentration of 10 mg/l. PHREEQC was then asked to reduce the dosage in an attempt to find an optimum rate where by the quality of the final discharge remained similar to that recorded at a dosage rate of 500 l/hr. Table 1 shows the raw water quality input into the PHREEQC model and Table 2 shows the results of the PHREEQC modelling at a reduced dosage rates of 180 mg/l and 160 mg/l. These dosage rates were still able to increase the pH from an initial pH of 6.6 to the target pH of 8.5.

**Table 1: Raw mine water quality at Frances colliery**

Variable	
Temperature (°C)	17
PH	6.6
Alkalinity (mg/L as CaCO <sub>3</sub> )	-
Ca (mg/L)	371
Mg (mg/L)	301
Na (mg/L)	405
K (mg/L)	29.2
Fe (mg/L)	31.8
S (6) (mg/L)	1750
Cl (mg/L)	625
CO <sub>2</sub> (g) – Atm Pressure	10 <sup>-3.5</sup>
O <sub>2</sub> (g) – Atm Pressure	10 <sup>-0.67</sup>

**Table 2: Modelled mine water using caustic soda**

Sample Date: 26/03/03			
	Model Concentration		Recorded Onsite Final Discharge Conc.
Ions	moles/l	mg/l	mg/l
Al	4.07E-06	0.11	0.12
Ca	9.26E-03	371.14	322
Cl	1.76E-02	623.92	648
Fe	5.69E-04	31.77	20.5
K	7.47E-04	29.21	28
Mg	1.24E-02	301.44	292
Mn	1.39E-04	7.64	6.36
Na	2.16E-02	496.58	477
S	1.82E-02	1747.20	1590

160 mg/l of NaOH was required in the 80 l/sec of mine water to increase the pH from 6.6 to 8.5

Note: Model used raw chemical data for 13/06/03 and instructed PHREEQC to dissolve NaOH into the raw water and predict the final discharge water quality.

<b>Sample Date: 13/06/03</b>				
	<b>Model Concentration</b>		<b>Recorded Onsite Final Discharge Conc.</b>	
<b>Ions</b>	<b>moles/l</b>	<b>mg/l</b>		<b>mg/l</b>
Al	3.71E-06	0.10		0.08
Ca	8.63E-03	345.89		246
Cl	1.50E-02	531.75		623
Fe	8.30E-04	46.35		78
K	6.27E-04	24.52		28
Mg	1.00E-02	243.10		261
Mn	1.30E-04	7.14		3.68
Na	1.77E-02	406.92		629
S	1.63E-02	1564.80		1680

180 mg/l of NaOH was required in the 80 l/sec of mine water to increase the pH from 6.22 to 8.5

Note: Model used raw chemical data for 13/06/03 and instructed PHREEQC to dissolve NaOH into the raw water and predict the final discharge water quality.

The PHREEQC geochemical model was able predict the final water, generally to within the 5 – 10% of those values recorded on site. However, PHREEQC predicted that the amount of caustic required to maintain this quality was almost an order of magnitude lower than that initially thought to be required to raise the pH to a value of 8.5. This prediction was later put to the test during the pump test as the caustic soda dosage rate was gradually reduced and it was found that the mine water at Frances Colliery could be effectively treated at a lower dosage rate than was previously thought. The final water quality remained in a similar range to that predicted. Therefore, it was decided that less alkali dosing would be required in future.

### 2.3 *Identification of secondary phase mineralisation*

During the pump test at Frances Colliery, it became apparent that a yellow/white secondary mineral or amorphous phase was rapidly precipitating on the surface of the pH probe and delivery pipework within the treatment plant. The system was becoming fouled within 4 hours of it being cleaned. Therefore, it was not possible to use the automatic dosing system to control the mine water pH.

The PHREEQC geochemical model was used in this situation to identify any possible secondary phases that could have been precipitating out of the mine water and on to the pipework and pH probe. By inputting the quality of the mine water into the model and adding the dosage of caustic being used at the time of the precipitation event, it was possible to list the likely secondary phase that could be causing the problem. According to the saturation indices determined by PHREEQC, the precipitate was likely to be either Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or Epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ). However, precipitation of Jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) could not be ruled out. Laboratory experiment conducted by Croxford, (2003), showed that it is possible for secondary amorphous phases to form in a solid solution state, where all three secondary phases could form as a solid mixture, rather than a pure form of just one. Unfortunately, it has not been possible to analyse a sample of this material to date, so we are unable to validate PHREEQC's prediction at present.

The use of PHREEQC to determine the possible formation of secondary phases during this project has illustrated how successful the model could be in pre-empting maintenance problems, such as fouling of pipe ranges and connectors, within current and future waste water treatment plants. This method of secondary phase prediction could aid in the minimisation of maintenance problems during the operational phase of the scheme.

## 3.0 **Horden Mine Water**

### 3.1 *Project description*

The Coal Authority, working in conjunction with Local Authorities, the Environment Agency and other interested parties, is working to develop a long-term strategy to control mine water in Durham. A long-term solution has not yet been finalised and temporary pumping and treatment system is required at Horden that will delay the recovery of the rising water. In this

way the water supply can be protected while a final system is designed and constructed.

The mine water pumped from the shaft at Horden contains increased levels of iron, which need to be reduced before the water is discharged into the sea. An active treatment system was proposed where mine water is pumped to the treatment plant using submersible pumps lowered down Horden South Shaft. The flow is split into 3 process streams, each with a rated capacity of 140m<sup>3</sup>/hr, giving a total capacity of 420m<sup>3</sup>/hr (117L/s) when all three streams are on-line or 280m<sup>3</sup>/hr (77L/s) when one of the streams is off-line for maintenance.

The mine water is initially aerated to strip any dissolved carbon dioxide prior to removing up to 200mg/l of dissolved iron. Based on the preliminary studies undertaken to date it is proposed to remove the iron using a two stage precipitation process designed to precipitate it in a manner that minimises the volume of sludge generated (this process is called the 'High Density Sludge Process'). The precipitated iron particles are separated from the treated water in a clarifier. Treated water is removed from the top of the clarifier into a final effluent sampling sump and discharged via gravity into the North Sea. Sludge is removed from the base of the clarifier and either re-circulated back to the Stage I Reactor Tank or transferred to a sludge holding tank.

Prior to the commencement of pumping at Horden, there were few details of anticipated mine water quality and this was based upon historic information. In order to provide some ideas on mine water quality, a series of hydrological surveys were carried out at open mine shafts in the area and at the same time, discrete samples of water in the shaft columns were taken for analyses. The water was found in most cases to be stratified, better quality of water at the top of the shaft column and worse quality nearer the bottom of each shaft. It is thought that this is because the upper layers of water are derived from the Permian that lies above the Coal Measures, rather than water that has been in intimate contact with pyritic material. This survey along with the investigation into likely flow paths also established the criterion for the temporary pumping arrangements. The quality of the water to be treated at Horden was uncertain as water pumped from the mine shaft will comprise a mixture of relatively clean surface water and deep iron laden brackish water. The plant was designed to treat any mixture of these two waters.



### 3.2 *PHREEQC prediction of sludge volumes and pH for various alkali reagents*

PHREEQC was successfully used during the outline design stage of the Horden mine water project. Initially the model aided the identification of the most effective and efficient alkali to be used in an active mine water treatment scheme. It was able to determine the quantity of alkali required to raise the pH from about 6 to between pH 8 and 8.5. Three different alkalis were used during the study. These were; caustic soda (NaOH), calcium hydroxide (Ca(OH)<sub>2</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). Some of the formulas for these alkalis were not present in the PHREEQC database. Therefore, alkali formulas and Log-K values selected from Stumm and Morgan (1996), were entered into the database. The alkalis were inputted into the PHREEQC model as equilibrium phases that could be precipitated or dissolved in accordance with environmental conditions.

As well as being able to calculate the quantity of each alkali required to raise the pH to between 8.0 and 8.5, it was also possible to utilise PHREEQC to estimate the likely volume of sludge generated by each of the three alkalis, during the active treatment process. Table 3 shows the quality of water from Horden, which was inputted, into the PHREEQC and Table 4 shows the quantity of each of the three alkalis required to raise the pH to between 8 and 8.5. It also shows the quantity of sludge expected to be generated during the used of each alkali.

***Table 3: Horden water quality (general mine water quality for design purpose only)***

Variable	
Temperature (°C)	17
PH	5.9 - 6
Alkalinity (mg/L as CaCO <sub>3</sub> )	0
Ca (mg/L)	2000
Mg (mg/L)	1000
Na (mg/L)	2000
K (mg/L)	1000
Fe (mg/L)	200
S (6) (mg/L)	3500
Cl (mg/L)	35000

CO <sub>2</sub> (g) – Atm Pressure	10 <sup>-3.5</sup>
O <sub>2</sub> (g) – Atm Pressure	10 <sup>-0.67</sup>

*Table 4: Alkali concentration and predicted pH and sludge volumes (dry weight)*

	<b>NaOH</b>	<b>Ca(OH)<sub>2</sub></b>	<b>Na<sub>2</sub>CO<sub>3</sub></b>
Conc. of alkali to reach target pH (g/l)	0.4	0.37	0.53
Predicted pH	8.27	8.23	8.24
<b>Sludge Volumes</b>			
CaSO <sub>4</sub> (t/yr)	2790	2760	2790
CaCO <sub>3</sub> (t/yr)	40	40	40
Ca(HCO <sub>3</sub> ) <sub>2</sub> (t/yr)	150	150	150
Total (t/yr)	2980	2950	2980

It is apparent from the modelling data that the total tonnage of sludge estimated to be generated each year through the use of all three alkalis is very similar. The likely volume of alkali required to raise the pH to the target range of between pH 8 and 8.5 is also very similar. However PHREEQC determined that the treatment scheme would use slightly lower quantities of Ca(OH)<sub>2</sub> than NaOH and Na<sub>2</sub>CO<sub>3</sub> to achieve the target pH range. The model also calculated the generation of slightly lower quantities of sludge using Ca(OH)<sub>2</sub> compared to the other two alkalis. Therefore, depending on price and availability, the PHREEQC model determined Ca(OH)<sub>2</sub> as the most logical choice in the treatment of mine water at Horden.

### *3.3 Predicted effect of increasing CO<sub>2</sub> partial pressure on alkali requirement.*

As the mine water in the pump shaft at Horden is expected to be at an initial depth of approximately 265m below OD it is expected that the partial pressure of the gaseous phases will vary as the mine water travels from depth to surface prior to treatment. One of the main concerns of treating a water from this depth is the effect of Partial Pressure on carbon dioxide gas (PCO<sub>2</sub>). This gas can dissolve in solution forming varying

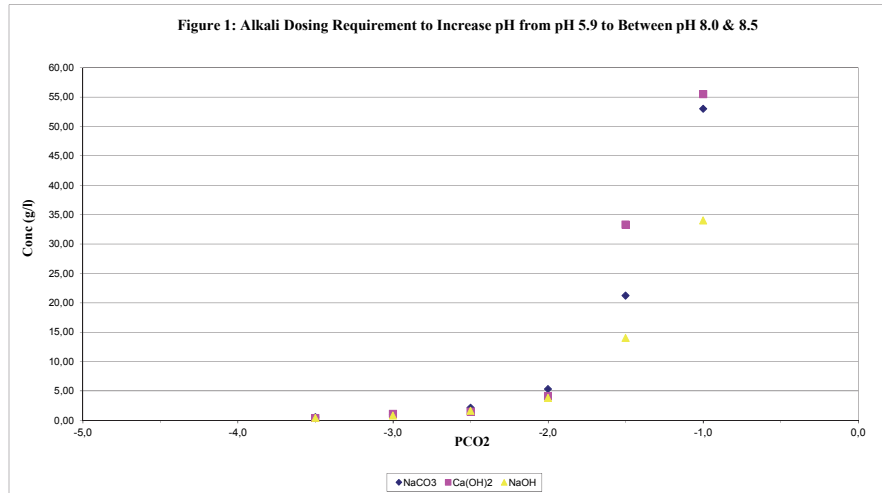
quantities of carbonic acid ( $\text{H}_2\text{CO}_3^*$ ), hydrogen carbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions, depending on the pH of the mine water. If the  $\text{pH} < 6.35$  elevated  $\text{PCO}_2$  partial pressure will result in increased (temporary) acidity as  $\text{H}_2\text{CO}_3^*$ . However, if the  $\text{pH} > 6.35$  the elevated  $\text{PCO}_2$  will contribute to alkalinity as  $\text{HCO}_3^-$ . If the partial pressure is high, it forces more carbon dioxide gas to stay in solution and if the pH of the mine water is also net acidic it encourages the pH to stay in solution in an acidic form. ( $\text{H}_2\text{CO}_3^*$ ).

Therefore, the pH is suppressed further as a result of the temporary acidity. As the mine water makes its journey from deep within the mine workings to the surface the pressure exerted on the gasses to stay in solution is reduced. This causes degassing within the mine water which subsequently results in a reduction of the temporary acidity. This variation in temporary acidity need to be considered when determining alkali dosage rates for treatment plants.

The PHREEQC geochemical was a valuable tool that was used in the determination of alkali dosage rates under varying carbon dioxide partial pressures. The model was asked to calculate the amount of alkali required to raise the mine water pH from about pH 6 to the target range of between 8.0 and 8.5 under varying  $\text{PCO}_2$  conditions. Figure 1 and Table 5 illustrates the quantities of each alkali that was required to ensure the pH was raised to within the target range of 8.0 – 8.5.

*Table 5: Predicted effect of increasing  $\text{CO}_2$  partial pressure on alkali requirement*

<b><math>\text{PCO}_2</math></b>	<b>Conc. of alkali required (g/l)</b>		
	<b>NaOH</b>	<b>Ca(OH)<sub>2</sub></b>	<b>Na<sub>2</sub>CO<sub>3</sub></b>
-3.50	0.40	0.37	0.53
-3.00	0.80	1.11	0.95
-2.50	1.60	1.48	2.12
-2.00	3.80	4.07	5.30
-1.50	14.00	33.30	21.20
-1.00	34.00	55.50	53.00



The  $PCO_2$  was gradually raised from atmospheric conditions ( $PCO_2 = -3.50$ ) to a maximum value of  $-1.00$ . The results of the PHRREQC modelling demonstrated a clear increase in the quantity of all three alkalis tested between  $PCO_2$  values of  $-2.00$  and  $-1.50$ . This implied the active treatment of mine water using alkali dosing is more efficient and cost effective if the mine water is initially allowed to degas and equilibrate with atmospheric gases. Therefore, it is beneficial to allow the mine water to be exposed to atmospheric conditions for a period of time prior to treatment.

Table 6 illustrates the likely mineral phases arising from treatment of the Horden shaft mine water under various pH and  $PCO_2$  conditions using the alkali NaOH (caustic soda) .

Table 6 – PHREEQC modelling results for Horden mine water under pH and pCO<sub>2</sub> conditions.  
(large positive numbers indicate higher likelihood of precipitation of mineral)

Target pH at Variable pCO <sub>2</sub>		8.35 and 10 <sup>-3.5</sup>	7.34 and 10 <sup>-3.5</sup>	8.37 and 10 <sup>-2.5</sup>	7.18 and 10 <sup>-2.5</sup>	8.37 and 10 <sup>-1.66</sup>	7.23 and 10 <sup>-1.66</sup>
[NaOH] required (mole L <sup>-1</sup> )		0.0050	0.0017	0.1000	0.0470	0.3000	0.0600
Saturation Indices (SI)	K-Jarosite, KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	<b>6.17</b>	<b>8.75</b>	<b>11.50</b>	<b>14.38</b>	<b>11.52</b>	<b>14.31</b>
	Goethite, FeOOH	<b>10.49</b>	<b>10.34</b>	<b>12.29</b>	<b>12.06</b>	<b>12.31</b>	<b>12.09</b>
	Amorphous Fe(OH) <sub>3</sub>	<b>4.86</b>	<b>4.70</b>	<b>6.66</b>	<b>6.43</b>	<b>6.67</b>	<b>6.45</b>
	Dolomite, CaMg(CO <sub>3</sub> ) <sub>2</sub>	2.99	-1.04	5.03	0.32	6.46	2.20
	Calcite, CaCO <sub>3</sub>	1.43	-0.59	2.45	0.09	3.14	1.03
	Aragonite, CaCO <sub>3</sub>	1.28	-0.74	2.30	-0.05	2.99	0.88
	Gypsum, CaSO <sub>4</sub>	-0.06	-0.05	-0.09	-0.06	-0.25	-0.07

Note: The initial pH of the mine water solution entered into the model was pH 5.9

According to PHREEQC, there was an increased likelihood of mineral precipitation as  $PCO_2$  increases. The model also indicated that there was a reduced chance of Ca and Mg carbonate precipitation at a lower pH (ca. 7.3). Once again PHREEQC has indicated that there would be an increase in the required volume of NaOH to raise the pH to the target range as  $PCO_2$  increases.

According to the calculated Saturation Indices for gypsum at under varying  $PCO_2$ , the secondary mineral phase was just below equilibrium ( $SI = 0$ ). Therefore, this mineral phase could precipitate out of solution if the environmental conditions were favourable. Some form of carbonate solid solution could also form depending on local conditions within the mine water solution.

From the PHREEQC modelling it was possible to determine that aeration of the mine water at Horden shaft would benefit the proposed mine water treatment scheme. This would minimise the amount of alkali required to increase the pH to between 8.0 and 8.5. It should also lower the dissolved  $CO_2$  content of the mine water and therefore, reduced the temporary acidity. The reduction in dissolved  $CO_2$  should also reduce the likelihood of carbonate precipitation, under certain environmental conditions.

### 3.4 *Determination of chloride concentrations of the precipitation of gypsum using PHREEQC*

IMC/ WYG were asked to investigate the influence of chloride concentrations on gypsum precipitation within mine water abstracted from the Horden shaft. Table 7 shows the initial water quality and atmospheric conditions that were used when running the PHREEQC model.

**Table 7: Water quality for Horden mine water sampled on 30/09/03**

Variable	
Temperature (°C)	17.5
PH	5.9
Alkalinity (mg/L as $CaCO_3$ )	17
Ca (mg/L)	1630
Mg (mg/L)	1020
Na (mg/L)	21822
K (mg/L)	2020
Fe (mg/L)	27.1

Al (mg/L)	0.37
Mn (mg/L)	2.06
S (6) (mg/L)	3860
Cl (mg/L)	35500
N (-3) (mg/L)	6.8
CO <sub>2</sub> (g)	10 <sup>-3.5</sup>
O <sub>2</sub> (g)	10 <sup>-0.67</sup>
Caustic soda (mole L <sup>-1</sup> )	0.0017

To investigate the possible influence of chloride concentration on gypsum precipitation, the chloride concentration was decreased in successive model runs by increments of 10,000 mg/l, whilst the remaining water chemistry remained the same. To maintain an overall charge balance sodium concentration was decreased by an equivalent amount (i.e. 6,480 mg/l). Table 8 summarises the results of the modelling at different chloride concentrations.

***Table 8: 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
<b>Gypsum saturation index</b>	<b>-0.02</b>	<b>0.03</b>	<b>0.11</b>	<b>0.24</b>

The results indicate that there is an increasing likelihood of gypsum precipitating as chloride concentration decreases. This implies that chloride may act to inhibit the potential for gypsum precipitation under certain environmental conditions. This information could be utilised and incorporated into the design of future waste water treatment schemes where there is a problem with excessive secondary phase precipitation.

#### **4.0 Conclusions**

This paper has demonstrated how geochemical modelling can provide invaluable information on the likely geochemical processes taking place prior to and during the treatment of waste water. Although the work conducted for this paper concentrated predominantly on mine waters, the same principles can be adapted for use with other contaminated waters. The PHREEQC predictive modelling could be used by developers, regulatory authorities and environment agencies to produce a management plan for potentially contaminant generating activities. Such a plan could enable industries to be controlled at optimum efficiency whilst causing minimal detrimental damage on the local, regional and global environment.

The costs associated with remediation are generally substantial. Therefore, it is necessary to consider whether the generated pollution could have been minimised through effective management. If developers had the ability to determine the potential extent of environmental pollution generated by their proposed development through the use of predictive geochemical models, they could anticipate the long-term costs involved in minimising and remediating any environmental impact caused.

Geochemical prediction models could be incorporated into a development's Phase I feasibility study to ensure that the proposed development scheme had considered the implications of contaminant loading of the environment during the initial, main and final stages of the project. Detailed consideration would also have to be given to the environment following completion of the project.

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