

# The Importance of Understanding the Implications of the Carbonate Balance on Active Mine Water Treatment

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### Abstract

The importance of carbonate chemistry and its role in passive mine water treatment is well understood and is supported by numerous publications (Hedin, Narin, Kleinmann 1994). However, there is less published information on its importance in active mine water treatment. In particular, the role carbonate chemistry plays in dictating alkali consumption and sludge generation

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#### Introduction

Studies on UK mines have shown that inorganic carbon dissolved and the corresponding carbonate chemistry has an important and often overlooked role in the active treatment of both net alkaline and acidic waters. Historically the differences between theoretical and measured alkali demand and sludge generation rates put down to process inefficiencies and/or parasitic "secondary reactions". In cases which Carbon dioxide (CO<sub>2</sub>) stripping has been incorporated in active plants, the benefits have typically been established experimentally, often without a full appreciation of the underlying chemistry. The purpose of this paper is to explore the importance carbonate chemistry in active mine water treatment and discuss how these "secondary reactions" can either be minimised or used advantageously.

Most active treatment plants operate with either one or two reactors with retention times of circa 20–40 mins to precipitate dissolved metals as metal hydroxides following the addition of an alkali with changes in the dissolved metal concentration and carbonate chemistry occurring simultaneously. This paper aims to demonstrate that by analysis the various carbonate reactions on an individual stepwise manner it is possible to:

• Assess the effect dissolved CO2 has on alkali demand and sludge generation

- Assess the effect metal precipitation on pH without alkali addition
- Predict calcium carbonate precipitation
- Demonstrate how the carbonate buffer can be used to reduce alkali demand and sludge generation.

# Method

By considering the carbonate  $CO_2/HCO_3^{-7}$   $CO_3^{-2}$  buffer reactions (Younger, 2002) along with pH, total inorganic carbon (TIC) and alkalinity it is possible to predict changes in the carbonate species and the effect these have on the plant performance. Knowing two of these parameters (pH and TIC for example) it is possible to calculate the remainder. For example, by assuming air stripping reduces the CO2 concentration to an assumed value, this together with the alkalinity value can be used to predict the pH and carbonate species concentrations. Fig. 1 illustrates how these vary for a process comprising the following treatment stages:

- Carbon dioxide air stripping (degassing)
- Iron precipitation using hydrogen peroxide (thereby avoiding the need to raise the pH to accelerate the iron oxidation reaction with oxygen)
- Raising pH to promote precipitation of other dissolved metals (such as manganese)
- Precipitation of these other metals and calcium carbonate



*Figure 1* Concentration changes for an iron and manganese removal process using CO2 stripping a hydrogen peroxide to promote iron oxidation and precipitation.

The application of this technique and its relevance to active treatment plant design is illustrated in the following 4 case studies.

### Case Study A – Highly Acidic Mine Water flowing from a Pyritic Orebody

This case study explores the treatment of a highly acidic mine water (pH circa 3). At the time of closure, the metal concentrations peaked at circa 5,000 mg/L iron, 200 mg/L zinc plus aluminium, cadmium and other metals. Immediately following closure an ad-hoc temporary treatment system was implemented, with the addition of lime slurry into the pipe carrying the water to the nearby tailings dam. Process control was implemented by manually checking the discharge pH and adjusting the lime addition accordingly. This simple process achieved 99.9% metal removal and has a lime efficiency of 85% (defined as the theoretical dose/actual dose).

Some 8 years later this process was replaced by a high density sludge (HDS) plant. To achieve the new manganese consent (< 1 mg/L) an operational pH > 9 was

required. At that point the iron concentration had reduced to around 200 mg/L. However, despite implementing the HDS process the lime efficiency had deteriorated to 72%. By 2024, the iron concentration had stabilised at around 80 mg/L and the lime efficiency had further deteriorated to less than 50%.

Whilst not in area dominated by carbonate geology, laboratory analysis revealed an average total inorganic carbon (TIC) concentration of 30 mg/L (which at the incoming pH 3 is present as dissolved CO2). On raising the pH to 9.3 to ensure manganese removal, the plant effectively acted as a lime softener precipitating the CO2 as calcium carbonate (Evans, Morgan, Coulton, 2019)

To confirm the implication of the dissolved CO2 on lime/alkali demand, an assessment of the changes in the carbonate chemistry with and without CO2 stripping was undertaken (as summarised in table 1)

The low mine water pH allows for a reduction of CO2 within the mine water without increasing the pH and concentration of bicarbonate ions resulting a best-case scenario for CO2 stripping. This data was

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	Fe <sup>2+</sup> mg/L	рН	TIC mg/L	CO <sub>2</sub> mg/L	HCO <sub>3</sub> - mg/L -	CO <sub>3</sub> <sup>2-</sup> mg/L	Alkalinity mg/L as CaCO <sub>3</sub>
Raw Mine Water	80	3	30	110	0	0	0
		Wit	hout CO <sub>2</sub> Strip	oing			
pH increase	80	9.3	30	0	138	12	135
Fe precipitation	0	9.3	301	0	138l	12	135
Calcium precipitation	0	9.3	0	01	0	01	0
		With	90% CO2 strip	ping			
Degassed	80	3	3	11	0	0	0
pH increase	80	9.3	3	0	12	1	13
Fe precipitation	0	9.3	3	0	12	1	13
Calcium precipitation	0	9.3	0	0	0	01	0

 Table 1 Case Study A - Predicted Carbonate Chemistry.

Table 2 Case Study A - Theoretical reduction in lime demand and sludge generation.

	Without CO <sub>2</sub> stripping	With CO <sub>2</sub> stripping	Predicted reduction
Lime demand	384 mg/L	219 mg/L	42%
Sludge generation	344 mg/L	222 mg/L	35%

then used to estimate the resultant changes in lime consumption and sludge generation that could be achieve by stripping 90% of the  $CO_2$  (as summarised in Table 2 below). Due to the elevated levels of calcium the addition of lime still has a softening effect but with a reduced precipitant volume.

# Case Study B – Treatment of a Net Alkaline Mine Water with and without CO2 stripping

In contrast to Case Study A this study considers the effect of  $CO_2$  stripping on a circum neutral net alkaline mine water. The plant was constructed over a decade ago to treat water containing 50 mg/L dissolved iron. And included a pre-treatment stage to air strip  $CO_2$ . After period of successfully operation, problems were encountered with the  $CO_2$  stripping stage, which was switched off and the HDS plant operated without the benefit of degassing.

This provided an opportunity to confirm the applicability of the stepwise methodology and compare the results with the actual plant performance. Table 3 summarises the predicted carbonate chemistry with and without CO, stripping. Table 4 provides a comparison of the predicted alkali/lime consumption for these two scenarios. In comparison the actual lime dose when the plant was operated without degassing was 290 mg/L (9% greater than the predicted value of 266mg/l).

Given the high influent alkalinity, it would be possible to operate the HDS plant using hydrogen peroxide as an oxidant rather than air (provided the treated water pH remained above lower consent limit of 6). Thereby avoiding the need for pH adjustment to accelerate the iron/oxygen kinetics. Table 5 summarises the predicted changes in the carbonate chemistry and the estimated final pH – which at 6.2 is still within consent. Importantly, whilst the unit price of hydrogen peroxide is more expensive that lime, it offers additional advantages in avoiding use of the CO<sub>2</sub> stripping mixers and blowers and potentially reducing the amount of sludge generated.

# Case Study C – Comparison of Predicted and Measured Values for a highly Alkaline Water

Case Study C relates to a former coal mine which following abandonment was allowed to flood and overflow at a rate of up to 200 L/s into the receiving watercourse. After



	Fe <sup>2+</sup> mg/L	рН	TIC mg/L	CO <sub>2</sub> mg/L	HCO <sub>3</sub> - mg/L -	CO <sub>3</sub> <sup>2-</sup> mg/L	Alkalinity mg/L as CaCO <sub>3</sub>
		With	hout CO <sub>2</sub> Strip	ping			
Raw Mine Water	50	6.4	174	300	467	0	382
pH Adjust + Fe precipitation	0	7.3	174	64	795	0.7	652
		With	80% CO2 strip	oping			
Raw Mine Water	50	6.4	174	300	467	0	382
Degassed	50	7.1	108	60	465	0.3	382
pH Adjust + Fe precipitation.	0	7.3	108	40	493	0.5	405

Table 3 Case Study B Predicted Carbonate Species.

Table 4 Table 4 Case Study B - Lime Consumption

	Predicted lime dose	Lime efficiency
With CO <sub>2</sub> stripping	83 mg/L	79.5%
Without CO <sub>2</sub> stripping	266 mg/L	25%

optioneering potential treatment solutions, it was decided that due to its location the only viable treatment option was active treatment using the HDS process.

Laboratory screening tests confirmed that to achieve the required dissolved iron and manganese concentrations of <1 mg/L it would be necessary to operate the plant at up to pH 9.3. At this pH, calcium carbonate precipitation will occur (increasing the alkali demand and sludge generation rate) making it critical to understand and control the carbonate chemistry. To provide meaningful process design data a 1m3/hr pilot plant (designed to replicate the HDS process) was mobilised to site to test a series of different treatment scenarios thereby optimising of the treatment process.

Table 6 contains a summary of the predicted carbonate species for each step of the proposed treatment process considering both the iron and calcium carbonate precipitation.

This data was used to predict both the lime consumption and sludge generation rates and comparison with pilot plant results as shown in Table 7. Lime/alkali demand from the pilot plant data was within 10% of the predicted values validating the calculation methodology. The predicted sludge generation at pH 7.5 is in reasonable agreement with the measured value, simply because at this pH very little carbonate precipitation takes place. However, at pH 9.3 the calculation over predicted the sludge generation as the methodology assumed all the calcium was fully precipitated. When back calculated using the measured residual calcium concentration the theoretical and actual values almost converge with the remaining difference possibly due to the short reactor residence time and the reaction kinetics.

# Case Study D Treatment of Mine Water from Net Alkaline Metalliferous Mine

This case study provides a comparison of the treatment options for a circum neutral mine water with elevated dissolved Iron, Arsenic and Manganese concentrations. This plant was required to treat water at a rate of 1050 m3/hr whilst achieving total arsenic and dissolved manganese concentrations of 50  $\mu$ g/L and 20  $\mu$ g/l respectively.

Pilot testing of a traditional HDS process demonstrated that consent compliance could only be achieved by coprecipitating all metal using calcium carbonate at pH10. This resulted in a lime demand of 296 mg/L and a sludge generation rate of around 400 mg/L (i.e. a daily lime consumption of 7.2tpd and a dry sludge maas of 10tpd some 100 m3/ day of sludge at the achieved settled solids concentration of 10%w/v).



Table 5 Case Study B Predicted i	Carbonate Species for Hydrogen	Peroxide based Iron precipitation.
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	Fe <sup>2+</sup> mg/L	рН	TIC mg/L	CO <sub>2</sub> mg/L	HCO <sub>3</sub> - mg/L -	CO <sub>3</sub> <sup>2-</sup> mg/L	Alkalinity mg/L as CaCO <sub>3</sub>
Raw Mine Water	50	6.4	174	300	467	0	382
Fe precipitation	0	6.2	174	375	360	0	295

*Table 6 Case Study C – Predicted Carbonate Species Distribution.* 

	Fe <sup>2+</sup> mg/L	рН	TIC mg/L	CO <sub>2</sub> mg/L	HCO <sub>3</sub> - mg/L -	CO <sub>3</sub> <sup>2-</sup> mg/L	Alkalinity mg/L as CaCO <sub>3</sub>
Raw Mine Water	45	6.15	165	370	324	0	266
Degassed	45	6.75	89	93	324	0	266
Iron out	0	6.35	89	163	226	0	186
pH increase	0	9.3	89	0.3	415	38	405
Calc precipitation	0	9.3	12	0	59	12	58.5

Further pilot testing to demonstrate the effect of CO<sub>2</sub> stripping revealed it was no longer possible to rely on this approach to achieve consent compliance. Instead, a two stage HDS process was developed with separate arsenic and manganese removal HDS circuits. Making use of the available carbonate buffer, this approach achieved iron coprecipitation of arsenic without the need for alkali addition. Table 8 shows the calculated stepwise approached used to calculate the chemistry changes. In comparison the actual reactor pH was 6.8. Importantly because the arsenic/iron removal stage did not require an increase in pH it was possible to concurrently precipitate the iron/arsenic whilst simultaneously stripping the CO<sub>2</sub> in a single reactor simplifying the process. (Morgan, 2024)

On leaving iron/arsenic HDS stage, the pH was raised to 10 in the secondary HDS circuit to precipitate the manganese. Table 9 summarises the measured alkali/lime demand and sludge generation rates for both the original traditional HDS circuit and subsequently adopted two stage HDS process. This clearly demonstrates benefit achieved by utilising the carbonate buffer in the first HDS circuit, with the lime demand and sludge generation rates reduced by 80% and 60% respectively.

#### Conclusion

The case studies presented above illustrate the benefits of process engineers using a simple stepwise methodology to understand and manage the carbonate chemistry when designing and optimising active treatment

	Degassing	pH Lime Demand			Sludge G	ieneration
			Actual	Theoretical	Actual	Theoretical
lron precipitation	Yes	7.5	130 mg/L	122 mg/L	100 mg/L	85 mg/L
lron + Manganese	Yes	9.3	≈ 400 mg/L	377 mg/L <sup>1</sup> 413 mg/L <sup>2</sup>	651 mg/L	657 mg/L <sup>1</sup> 814 mg/L <sup>2</sup>
precipitation	No	9.3		841 mg/L <sup>2</sup>		1.324 mg/L <sup>2</sup>

*Table 7* Case Study C Comparison of Theoretical and Actual Pilot plant Results.

Notes

<sup>1</sup>Calculated using the measured residual Calcium concentration of 58.5 mg/L

<sup>2</sup>Calculated on the assumption that all the calcium is precipitated as calcium carbonate

	Fe <sup>2+</sup> mg/L	рН	TIC mg/L	CO <sub>2</sub> mg/L	HCO <sub>3</sub> - mg/L -	CO <sub>3</sub> <sup>2-</sup> mg/L	Alkalinity mg/L as CaCO <sub>3</sub>
Raw Mine Water	33	6.3	35.6	69.1	85.4	0	70.0
Degassed	33	7.0	20.5	13.8	85.3	0	35.6
Iron out	0	5.5	20.5	65.0	13.7	0	11.1

**Table 8** Case Study D – Theoretical Carbonate balance for simultaneous carbon dioxide stripping and ironprecipitation with hydrogen peroxide oxidation

*Table 9 Case Study D – Reduction in lime demand and sludge generation achieved by beneficially using the carbonate buffer* 

	Original HDS concept without CO <sub>2</sub> stripping and use of carbonate buffer	Two stage process with CO <sub>2</sub> stripping and beneficial use of carbonate buffer
Lime Demand	296 mg/L	59 mg/L
Sludge generation	400 mg/L	162 mg/L

systems. As degassing with the short retention times available can only remove dissolved CO<sub>2</sub>, in low pH net acidic mine water degassing alone can provide a vast reduction of inorganic carbon. In circum neutral and net alkali water degassing can only remove a proportion of the inorganic carbon with reactions of bicarbonate ions raising the pH and limiting further CO<sub>2</sub> removal. Importantly the methodology shows in these cases where sufficient alkalinity is available the use hydrogen peroxide (instead of air/ oxygen) for iron oxidation and precipitation can remove the need for alkali addition offering potential significant cost saving in terms of reduced process complexity and operating cost.

#### References

- Hedin, R, Narin, R, Kleinman, R, (1994). Passive Treatment of Coal Mine Drainage, US Department of The Interior – Bureau of Mines Circular
- Younger, P, Banwart, S, Hedin, R, (2002). Mine Water – Hydrology, Pollution, Remediation. ISBN – 978-1-4020-0137-6
- Evans, J, Morgan, R, Coulton, R, (2019). The Effects of Using Hydrogen Peroxide to Provide an Improved HDS Process, 14th IMWA Congress (postponed) – Mine Water Solutions, p152–15
- Morgan, R, Coulton, R, Kingstone K, Watson N, (2024). Development of a single stage High Density Sludge (HDS) process for the reopening of South Crofty Tin Mine, Cornwall, UK, 15th IMWA Congress Proceedings of the International Mine Water Association Conference & West Virginia Mine Drainage Task Force Symposium, p452