

# MINERALOGICAL EXAMINATION OF CARBONATES IN THE CRANDON TAILINGS

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## ABSTRACT

Mineralogical analyses of carbonates in depyritized tailings and pyrite concentrate (from depyritization of the tailings) were completed as part of the tailings characterization for the Crandon Project, a massive sulfide deposit in northeastern Wisconsin. The mineralogical study was designed to determine the proportion of calcium and magnesium carbonates, and therefore the effective buffering capacity of carbonates in the tailings. The depyritized tailings are net acid consuming and will be stored in a surface tailings management area. The pyrite concentrate is net acid generating and will be used as backfill in the underground mine workings.

The majority of carbonates in the depyritized tailings were ferroan dolomite containing 10 to 15% iron (by weight) and lesser amounts of siderite and magnesian siderite. The proportion of calcium and magnesium-rich carbonates corresponds to several independent tests of carbonate neutralization potential (CO<sub>3</sub>-NP) availability. The pyrite concentrate had less CO<sub>3</sub>-NP, indicating segregation of the carbonates during pyrite flotation. These carbonates reported higher iron contents, consistent with the relatively lower availability of CO<sub>3</sub>-NP in the pyrite concentrate.

## INTRODUCTION

“Neutralization potential” (NP) is broadly defined as the capacity of waste rock or tailings to neutralize acidity. Measures of NP are generally compared to measures of acid generation potential, i.e. the capacity of these materials to produce acidity when exposed to water and oxygen, in order to determine whether the material is likely to be a net source or sink for acidity. The most commonly used methods for determining NP are the “Sobek” or “Modified Sobek” methods. These methods use a chemical titration to measure the total NP of the sample. Their main weakness is that they do not distinguish between the NP that would be reactive at neutral pH (e.g. carbonates) and the NP that would only be reactive after the onset of acidic conditions (e.g. silicates).

An alternative method that has been applied in recent years is measurement of carbonate-NP (Price 1997). Carbonate-NP or “CO<sub>3</sub>-NP” refers to the fraction of the NP determined either by direct measurement of the carbonate content of a sample, or (more typically) by calculation from the measured inor-

ganic carbon content. The advantages of this method are that it is relatively inexpensive, easily measured, and it does not consider any NP that would only be reactive at acidic pH (i.e. unlike Sobek NP). However, some types of carbonates (eg. siderite) are not capable of buffering acidity (Jambor et al. 2000; Lapakko 1994), while other types may not readily dissolve or react under neutral pH conditions (eg. magnesian siderite). A good understanding of the carbonate mineralogy is therefore important when estimating NP from carbonate content.

The most common types of carbonate minerals in most ore deposits are calcite, dolomite, ankerite and siderite (Alpers et al. 1994). However, several other carbonate phases, solid solutions and chemical substitutions have been identified at mine sites. Calcium and magnesium carbonates are considered to

be the most important for neutralization of acidity (Price 1997). In contrast, iron carbonates, such as siderite, do not provide any net buffering potential due to the oxidation of iron following dissolution of the carbonates (Jambor et al. 2000; Lappako 1994; and Skousen 1997).

The proportion of carbonates that will provide buffering is thought to be directly correlated to the calcium + magnesium content of the carbonates. For example, limestone (calcite) with 5% iron (atomic percent) in its structure would theoretically provide 95% of the buffering capacity of pure limestone. The importance of mineral form is less well understood, but may play a role in understanding the effectiveness of carbonate buffering. The well known fizz test used to identify carbonate minerals in the field is an example of this process, and suggests that minerals with calcite

or dolomite structures are more reactive under weakly acidic conditions than minerals with more resistant ankerite or siderite structures.

Calcium and magnesium carbonate-NP or "(Ca+Mg)CO<sub>3</sub>-NP" cannot be measured by any single analytical procedure, but can be estimated by combining a direct measurement of a sample's CO<sub>3</sub>-NP (or carbonate mineral content) with the quantification of the fraction of calcium and magnesium in the carbonate minerals.

In the following discussion, methods to characterize the (Ca+Mg)CO<sub>3</sub>-NP in tailings are demonstrated in studies undertaken as part of the waste characterization program for the Crandon Project. The Crandon Project is a massive sulphide zinc copper deposit in northern Wisconsin. Nicolet Minerals Company (NMC), is proposing to depyritize the tailings to produce a non-acid generating tailings product that will be placed in a composite lined surface impoundment or tailings management area (TMA). The resulting pyrite concentrate will be amended with cement, and placed as paste backfill in the mined-out underground stopes. Detailed testing of the depyritized tailings, pyrite concentrate and pyritic paste backfill has been completed as part of the waste characterization studies for this project (SRK 1999/2000a,b). The testing has included acid base accounting and detailed mineralogical analyses to determine the content, type and composition of the carbonates.

## METHODS AND MATERIALS

Tailings samples were prepared from a representative master composite of ore samples from the zinc ore zone of the deposit (SRK 1999/2000c). Metallurgical testing was completed at SGS Lakefield in Ontario using bench scale locked cycle flotation testing methods (Lakefield 1998a). From this, a bulk zinc tailings product was produced and used to test the amenability of the tailings to depyritization, also by froth flotation. Using the products from the locked cycle test, depyritized tailings with a target sulfur content of 0.85% and a pyrite

concentrate with a target sulfur content of 42% were produced.

Acid base accounting tests using both the modified Sobek method and carbonate analyses for NP determination were completed at SGS Lakefield (SRK 1999/2000a).

Initial mineralogical characterization of the carbonates included petrographic and X-ray diffraction (XRD) analysis on bulk samples of the depyritized tailings and pyrite concentrate, and semi-quantitative (SSQ) determination of the composition of the carbonate minerals by energy dispersive spectral (EDS) analysis (Lakefield 1998b; SRK 1999/2000a). A total of 9 randomly selected carbonate grains in the depyritized tailings sample, and 8 randomly selected carbonate grains in the pyrite concentrate sample were analyzed using this method.

A more detailed study on the carbonate mineralogy using electron microprobe (EMP) analysis was initiated to obtain quantitative data on the proportions of the different carbonate types and to improve the accuracy of the chemical analyses. This study was completed using an electron microprobe. The microprobe analyses were performed at CANMET Laboratories under a subcontract to SGS Lakefield, using a JEOL 8900 electron microprobe (Lakefield 1999; SRK 1999/2000c).

Analyses were completed on 60 carbonate grains from the depyritized tailings sample and 60 carbonate grains from the pyrite concentrate sample, including most of the grains previously analysed by SSQ (five from the depyritized sample and seven from the pyrite concentrate).

## RESULTS

The acid base accounting results are provided in Table 1. The results indicate that the depyritized tailings have a CO<sub>3</sub>-NP of 89.6 kg CaCO<sub>3</sub> eq./tonne, while the pyrite concentrate has a CO<sub>3</sub>-NP of only 15.9 kg CaCO<sub>3</sub> eq./tonne.

The XRD analyses indicated that the depyritized tailings contain minor

amounts of dolomite. Dolomite was not detected in the pyrite concentrate.

The initial SSQ-EDS analyses determined that the majority of the carbonates in the depyritized tailings are ferroan dolomite. Carbonates in the pyrite concentrate include ferroan dolomite, siderite and an iron zinc carbonate. The composition of the ferroan dolomite was approximately 83% calcium+magnesium.

The results of the microprobe analyses are summarized in Tables 2 and 3. The results confirm that ferroan dolomite is the primary carbonate mineral in the depyritized tailings, comprising 90% of the carbonate grains. In contrast, ferroan dolomite accounts for only 43% of the carbonate grains in the pyrite concentrate. Other carbonates identified in the pyrite concentrate were iron-rich magnesian siderite and siderite.

Ferroan dolomite had an average calcium+magnesium content of 88±3.4% in the depyritized tailings, and 83±18.3% in the pyrite concentrate, with the balance made up of iron, manganese and trace amounts of zinc.

## DISCUSSION

The relatively high detection limit of XRD analysis (0.5-2 wt.%, dependent on crystallinity) did not allow for identification of small quantities of carbonate in the pyrite concentrate. Only semi-quantitative energy dispersive spectral (SSQ-EDS) and electron microprobe (EMP) analysis were able to quantify and characterize these minerals.

A comparison of the SSQ-EDS and EMP results is provided in Figure 1. Only data from grains analyzed by both methods are shown. The comparison indicates that the SSQ-EDS method was suitable for identification of the bulk grain composition. Although SSQ-EDS analyses of composition tended to underestimate calcium and iron contents, and over-estimate magnesium contents, all of the SSQ-EDS values were within 10% of the EMP values. This suggests that the more widely available SSQ-EDS method is adequate for determining the elemental composition of the carbonates.

Table 1. Acid Base Accounting Results for the Depyritized Tailings

SAMPLE ID	PASTE pH S.U.	SULFUR (T) %	CO <sub>3</sub> %	Sobek NP <sup>1</sup>	CO <sub>3</sub> – NP <sup>1</sup>	AP <sup>1,2</sup>	NNP <sup>1</sup>	Sobek NP/AP	CO <sub>3</sub> -NP/AP
Depyritized Tailings	6.74	0.79	5.38	75.3	89.6	24.5	50.8	3.1	3.7
Pyrite Concentrate	5.55	40	0.95	16.2	15.9	1250	-1234	0.01	0.01

Notes: NNP - Net Neutralization Potential; AP - Acid Generation Potential

<sup>1</sup> Units for all NP, AP and NNP are kg CaCO<sub>3</sub> eq/tonne.

<sup>2</sup> AP calculated from total sulfur.

Table 2. Electron Microprobe Analysis of Carbonates on the Depyritized Tailings

CARBONATE MINERALS	CARBONATE DISTRIBUTION %	AVERAGE COMPOSITION (ATOMIC PERCENT)				
		Ca	Mg	Fe	Mn	Zn
Ferroan Dolomite	90	50±0.9	38±2.5	9.6±4.7	2.5±1.1	<0.1±0.02
Magnesian Siderite	8.5	0.36±0.17	35±7.9	60±7.3	4.0±2.1	<0.1±0.03
Ferroan Magnesite	1.7	0.048	84	14	1.7	<0.1
Weighted Avg.		0.30	43	53	3.6	<0.1

Table 3. Electron Microprobe Analysis of the Carbonates in the Pyrite Concentrate

CARBONATE MINERALS	CARBONATE DISTRIBUTION %	AVERAGE COMPOSITION (ATOMIC PERCENT)				
		Ca	Mg	Fe	Mn	Zn
Ferroan Dolomite	43.3	52±9.6	31±8.7	15±6.5	2.7±1.2	<0.1±0.09
Magnesian Siderite	23.3	0.58±0.49	32±11.3	62±11.1	4.5±2.9	<0.1±0.05
Siderite	33.3	2.7±1.4	4.0±2.2	87±4.3	2.8±1.1	3.6±3.6
Weighted Avg.		1.8	16	77	3.5	2.1

The overall or "total" calcium and magnesium fraction of all the carbonates, including calcium and magnesium in the magnesian siderite and ferroan magnesite in the depyritized tailings was 84%. The "dolomitic" calcium+magnesium fraction of the carbonates was on the order of 79%. The main implication of these results is that the approximately 79 to 84% of the carbonates in the depyritized tailings are capable of neutralizing acidity produced by sulphide oxidation. At a CO<sub>3</sub>-NP:AP ratio of 3.7:1, the corresponding (Ca+Mg) CO<sub>3</sub>-NP:AP ratio is 2.9:1, indicating there is a considerable excess of effective calcium+magnesium carbonate NP available to neutralize acidity generated during sulphide oxidation.

Long-term humidity cell tests have been operating since July 1998 to demonstrate that neutral conditions would be maintained in the depyritized tailings indefinitely, (i.e. the sulphide content would be depleted through oxidation before the carbonate minerals have fully reacted or been leached from the system). Additional humidity cell tests with higher amounts of sulphide have been initiated to obtain more accurate estimates of the true availability of the carbonate-NP.

Interim estimates of the available CO<sub>3</sub>-NP can be made on the basis of several other tests that have been carried out over the course of the Crandon Project. These include acid

neutralization humidity cell tests and humidity cell tests on tailings that contained much higher sulphide concentrations, and "multiple step batch tests" on depyritized tailings that were completed under mildly oxidizing and anoxic conditions (SRK, 1999/2000d). The estimates of the available CO<sub>3</sub>-NP ranged from >29% to 76%, with three of the four results in the range of 66% to 76%. These estimates are approaching the calcium+ magnesium content of the carbonates, suggesting that (Ca+Mg) CO<sub>3</sub>-NP is a good predictor of the neutralizing potential that will actually be available under field weathering conditions. Further results from the humidity cell tests are needed to verify this conclusion.

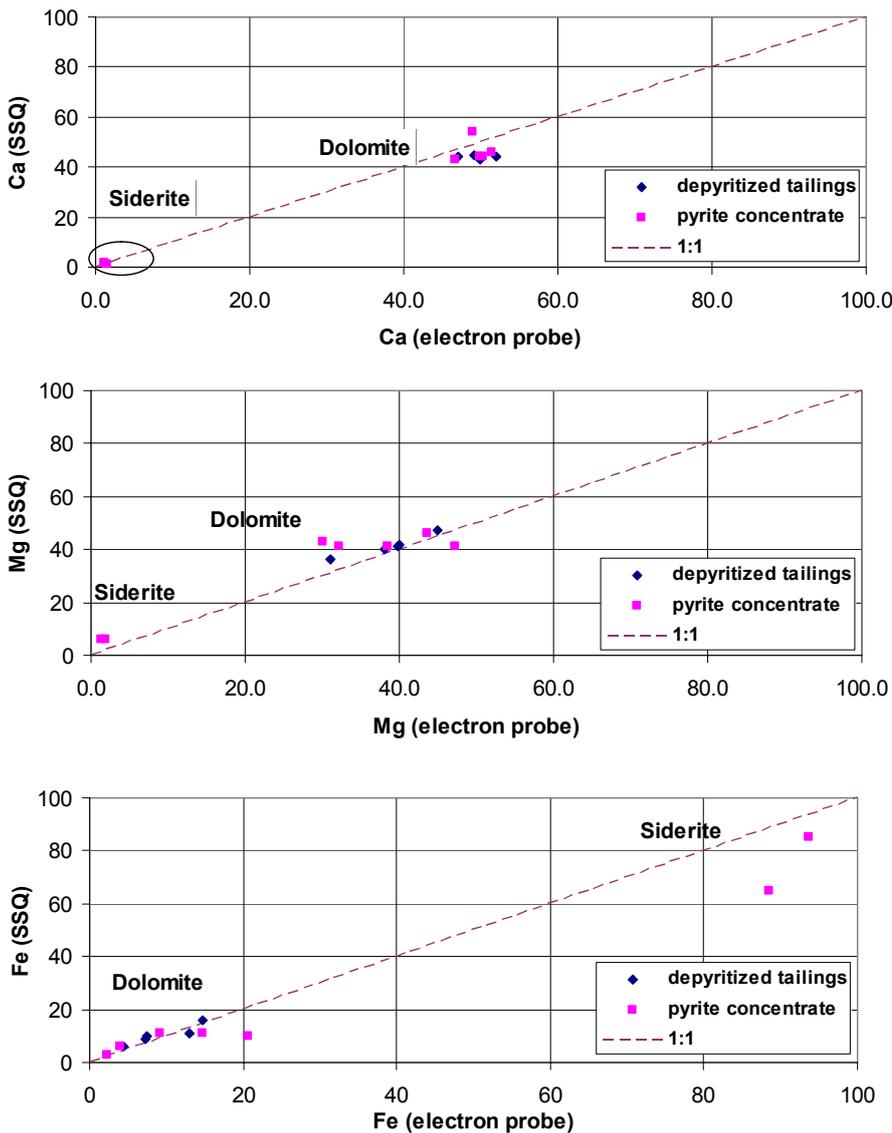


Figure 1. Comparison of SSQ-EDS and EMP Analyses

A much smaller portion (43% overall and 36% as dolomitic  $(Ca+Mg)CO_3$ -NP) of the carbonates in the pyrite concentrate was present as calcium+magnesium carbonate. The NP present in the pyrite concentrate will be supplemented in part by the addition of cement. The carbonate and cement derived NP will result in a delay of the onset of acidic conditions (60 weeks in humidity cell tests). Continuous placement of backfill and then limited oxygen entry into the cemented backfill with specifically designed and built structures will prevent acidification of significant proportions of the pyrite backfill during operations. On closure, flooding of the backfill will prevent acid generation in the long-term.

The observation that depyritized tailings had a much higher proportion of ferroan dolomite than the pyrite concentrate is thought to be due to selective concentration of the iron-rich carbonates in the pyrite concentrate during pyrite flotation. The segregation of iron rich carbonates is an unexpected benefit of the depyritization process. This effect may allow a more direct correlation between the carbonate content and the  $(Ca+Mg)CO_3$  NP in the depyritized tailings and may therefore simplify the monitoring programs that will be required to ensure that sufficient excess calcium+magnesium carbonate-NP is present in the tailings. Operational monitoring will provide further insight into this process.

## SUMMARY AND CONCLUSIONS

Semi-quantitative energy dispersive spectral (SSQEDS) or electron micro-probe (EMP) analyses are needed to accurately identify the carbonate minerals, and to determine their elemental composition. The more widely available SSQ-EDS method is sufficiently accurate for this purpose.

Ferroan dolomite comprises approximately 90% of the carbonates in the depyritized tailings and 43% in the pyrite concentrate. The calcium + magnesium content of the ferroan dolomite typically ranges from 84% to 90%. Other carbonates identified in the samples include magnesian siderite and siderite. The iron rich carbonates are typically more concentrated in the pyrite concentrate. This is attributed to selective concentration of the iron carbonates during pyrite flotation. Segregation of the iron rich carbonates may simplify monitoring of the NP during operations.

The calcium+magnesium content of the "dolomitic" carbonates is on the order of 79% for the depyritized tailings, and 36% for the pyrite concentrate. The "total" calcium and magnesium content of the carbonates, including magnesian siderite and ferroan magnesite, is 84% in depyritized tailings and 43% in the pyrite concentrate. The use of  $(Ca+Mg)CO_3$ -NP as a predictor of available neutralization potential is supported by testing to date, but requires confirmation in ongoing humidity cell tests. The  $(Ca+Mg)CO_3$ -NP:AP ratio for the depyritized tailings is approximately 2.9:1, indicating that acidic conditions will not develop.

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<sup>1</sup> Several of the consultants reports listed below are filed with the Wisconsin Department of Natural Resources. They are available for review at the agencies Madison Wisconsin office.

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