Prediction of Acid Rock Drainage (ARD) from Calculated Mineralogy

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ABSTRACT

The acid-forming potential of ore and waste can be calculated based on a detailed knowledge of mineralogy, especially sulphide and carbonate contents. However, most mineralogical techniques (e.g., semi-quantitative X-ray diffraction (qXRD), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) point counting) are too expensive for routine application. Mineralogy can be calculated from assay data using linear programming (simplex method) which is a mature method with application to real world quantities that cannot be negative. In order to apply this method, a table of mineral compositions is required for all the significant minerals in the study area. Unlike least squares methods, the mineral list can exceed the number of elements included in the assay data. Several carbonate compositions with a range of neutralising potential can be included. To use the linear programming method, a calibration must be established based on known compositions. This calibration can be based on qXRD or SEM/EDS point counting methods.

Not all types of assay data are sufficient for calculating mineralogy reliably. The best assay data comes from X-ray fluorescence analysis of major elements, including "loss on ignition" (LOI). Adding measured C content to this analysis provides a robust data set for calculating sulphide and carbonate contents of rocks. The mineralogy can be calculated without measured C, if LOI and SiO_2 are included in the analysis. However, typical mine databases contain multi-element assays based on a four-acid digestion method. In this case SiO_2 is not analysed and there is no "LOI" or total C. With typical four acid digestion data it is not possible to estimate the original carbonate content even when the mineralogy is simple. In rocks with complex mineralogy, mixed carbonates and/or multiple sulphides, qXRD and full chemical analyses are required to calculated acid rock drainage potential from mineralogy.

Keywords: calculated mineralogy, linear programming, ARD, carbonate

INTRODUCTION

In mining operations, the rock mineralogy is a key parameter controlling the acid generation/neutralisation potential (Paktunc, 1999). An efficient measurement of mineral abundance in waste samples is the key to understanding large scale acid rock drainage (ARD) potential. This can be done via calculated mineralogy and there are a number of methods that can be used to determine modal mineralogy from chemical assay. Two of these methods with potential application in the minerals industry are discussed here. These methods have been applied to two data sets, one with a simple mineralogy and a second data set from rocks with multiple sulphide and carbonate minerals.

METHODOLOGY

There has been a long history of calculating mineralogy from assay data. An early version was Bryan et al. (1969) which was improved on by Le Maitre (1981) and a more recent version was published by Paktunc (1998, 2001). All of these programs are based on simple least squares models and thus suffer from two serious limitations: 1) The nature of least squares models requires the number of minerals to be less than the number of elements in the analyses, and 2) the methods used do not enforce non-negativity constraints, so often the calculated mineralogy is impossible. The standard method for calculating a least squares model with non-negative constraints was published by Lawson and Hanson (1995). However, this method can now be readily carried out using the non-linear minimization routine included in the "Solver" tool within EXCEL®; an easily accessible version of this was presented by Herrmann and Berry (2002).

There is an additional problem with simple least squares minimisation methods, in that these methods assume that the errors on all input data are the same in absolute terms. For example, the absolute errors on SiO_2 and CO_2 values are considered to be the same. In practice, the relative errors are similar so that high abundance elements such as SiO_2 are over fitted and low abundance elements such as S and CO_2 are under fitted. A better result is obtained if the fit errors are weighted by the measurement errors (Press et al., 1986). This is especially important when merging data with very different errors such as quantitative Xray diffraction (qXRD) and assay data. Berry et al. (2011) addressed these problems and suggested two solutions suitable for calculation of mineralogy applicable to mine wastes: weighted least squares and Linear Programming.

There are many choices involved in selecting the most suitable assay data set for a mining environment. We have carried out a full major element analysis (including Ba and Cu) by X-ray fluorescence (XRF) with associated measurement of "loss on ignition" (LOI). H_2O+ and CO_2 were measured using a Flash Elemental Analyser. No organic C was observed so all C is assumed to be in carbonate. Quantitative XRD results were obtained using SiroQuant™ ver3.0 using the Rietveld method which is a standardless, full pattern approach to semi-quantitative phase analysis.

In most cases mine assays do not included any estimate of the volatile components. In addition it is now common for multi-element data to be four-acid digestions where SiO_2 is not analysed. To show how the absence of these components in the analyses affects the accuracy of the calculation, the mineralogy was calculated from several different subsets of this data.

All results reported here are based on 50 samples. For the linear programming, a separate group of 50 samples was used as a training set. No samples from the training set were included in the test data. The mineralogy of the training set was estimated using the weighted least squares method and all available analytical data.

Weighted least squares to combine assay and qXRD results

The assay data alone do not include enough constraints to calculate complex mineralogy. One way to overcome this problem is by measuring the mineralogy by qXRD. The qXRD results provide many additional constraints that can be used in calculated mineralogy and the calculation can include all major minerals. In the examples reported here, we calculated the abundance of 26 distinct mineral compositions with 34 constraints. Berry et al. (2011) applied this technique using the "NNLS" (non-negative least squares) subroutine of Lawson and Hanson (1995). Here we have used the non-linear "Solver" routine in EXCEL®. All calculated mineral abundances were limited in the Solver routine to be ≥0 (non-negative constraint) and ≤100% (as required by closure constraints on modal abundance).

For the assay results the measurement error was estimated as 3% relative plus 0.05% absolute. The errors for the qXRD results are based on repetitions of samples, error estimates reported in the literature and consideration of the fit errors achieved. For qXRD results the errors were set at 6% relative plus 0.5% absolute. At this weighting the problem can be stated as finding a modal mineralogy consistent with the chemical analysis which is as close as possible to the qXRD results. All samples in this study could be adequately explained (chi-squared probability of valid fit greater than 25%) based on these error estimates.

Linear programming and the Simplex Method

The second method of calculating the modal mineralogy from chemical analyses suggested by Berry et al. (2011) was linear programming using the Simplex method (Press et al., 1986). For the results reported here, the calculations were carried out using the linear routine in "Solver" with EXCEL®. This method requires a training set to calibrate the objective functions required. It can calculate mineral modes from an extended mineral list and additional linear constraints can be added as required. In this method, as in the weighted least square method, calculated mineral abundances were limited to ≥0 and ≤100%. For some minerals additional upper limits to abundance were enforced. A list of 45 distinct mineral compositions was included in the calculation.

Experimental Data

Experiment A: Simple assemblage

An evaluation program has been run on samples from a Cu porphyry deposit with a relatively simple mineralogy where carbonate is dominated by calcite and the significant sulfides are pyrite and chalcopyrite. Extensive mineral liberation analyzer (MLA) measurements failed to detect dolomite, ankerite or siderite above detection levels.

For these samples the mineralogy was calculated by:

    a) weighted least squares using qXRD, major elements, total C and H_2O+

    b) linear programming using major elements, total C and H_2O+

    c) linear programming using major elements and LOI

    d) linear programming using major elements except SiO_2

For experiment A the weighted least squares results were used to calculate the preferred "best" values for acid generating potential (AP) and neutralising potential (NP).

Experiment B: Complex assemblage

In the second experiment, the deposit type was IOCG (iron oxide-copper-gold) and the mineralogy relevant to ARD is more complex. Calcite, siderite, dolomite and ankerite were detected at significant and highly variable levels. Sulphides include significant chalcocite, bornite and chalcopyrite as well as pyrite which was at relatively low levels (i.e., typically less than 1%). In many ways this represents a worst case scenario for calculating ARD potential from assay data. The only significant sulphate was barite so problems with estimating other sulphates were not tested. Because of the mineralogical complexity, the mineralogy of all samples was measured using a SEM/EDS point count method (20,000 points) on grain mounts (Fandrich et al., 2007).

For these samples the mineralogy was estimated by:

    a) SEM/EDS point counting

    b) weighted least squares using qXRD, major elements and LOI

    c) linear programming using major elements and LOI

    d) linear programming using major elements except SiO_2

The linear programming estimates of the carbonate minerals, in experiment B, were calculated as end-member compositions for calcite, dolomite and siderite. Since the preferred estimate of acid neutralising capacity from intermediate carbonates is a linear sum of the cations (Paktunc, 1999), no attempt was made to estimate the actual proportion of ankerite in these analyses. For experiment B the SEM/EDS point count data were used to calculate the preferred "best" values for AP and NP.

Since the application of interest here is prediction of ARD, the results will be discussed in terms of AP and NP. No pyrrhotite was detected in these samples so AP is primarily due to pyrite. Thus the AP was calculated simply, as suggested by Paktunc (1999):

$$AP = 16.33 * X pyrite \quad \text{in kg sulfuric acid equivalent per tonne}$$

The NP was calculated using the factors listed in Table 1.

Table 1 Estimates of NP from the literature (Skousen et al., 1997, Jambor et al., 2003, 2006, 2007, Hammarstrom et al., 2003). Siderite NP is for end-member siderite based on non-oxidisable cations as recommended by Paktunc (1999). All sulphides, tourmaline, fluorite, titanite and barite are assumed to have an NP of 0.
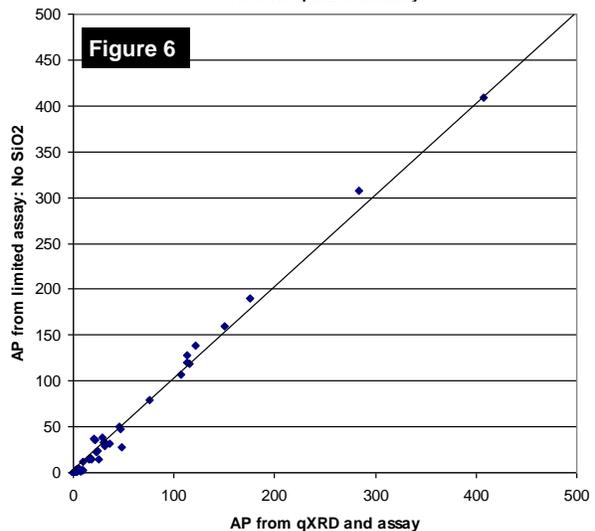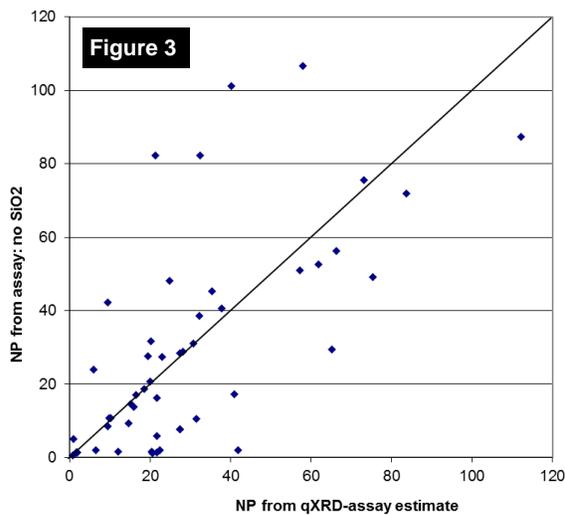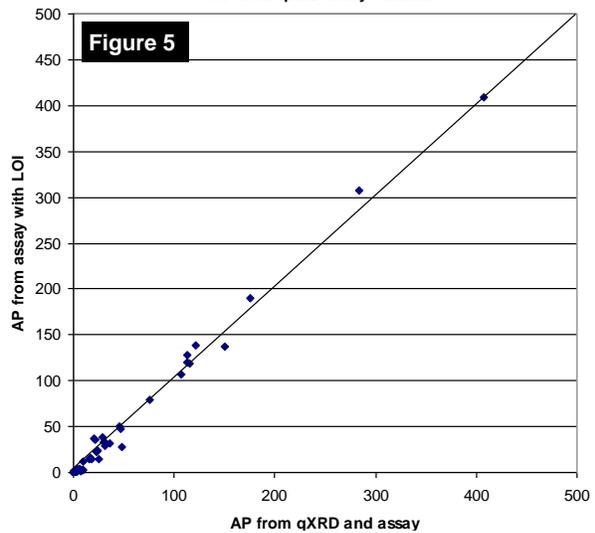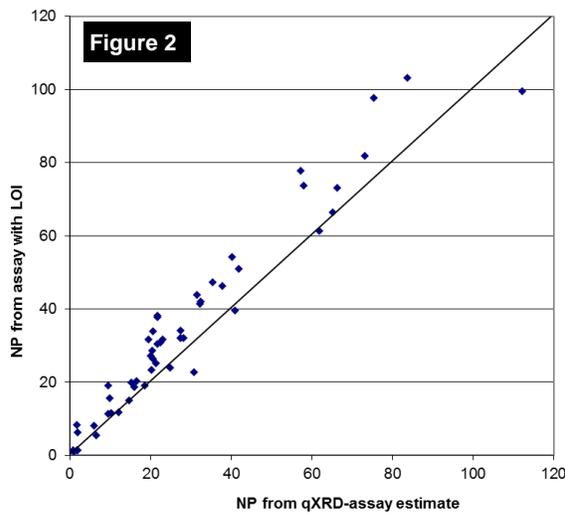
mineral	NP (calcite eq Kgms/t)	mineral	NP (calcite eq Kgms/t)
amphibole	3	K feldspar	1
ankerite	970	magnetite	2
apatite	8	muscovite	1
biotite	4	plagioclase	1
calcite	1000	pyroxene	5
chlorite	6	quartz	0
dolomite	1086	rhodochrosite	870
epidote	1	rutile	0
hematite	2	siderite	0
kaolinite	0		

RESULTS AND DISCUSSION

Experiment A: Simple assemblage

The abundance of calcite totally controls the NP results in experiment A. In this environment any method that considers the CO_2 content will produce an accurate assessment of the NP (Fig. 1). Where there is only a general indication of the volatile content, in this case a measure of LOI, the carbonate content can still be inferred but in these experiments the estimate is about 20% (relative) too high (Fig. 2). Using only the commonly available limited assay data, with no SiO_2 or LOI, the estimate is poor (Fig. 3) but still perhaps of some value as a general indication of which rock packages have acid neutralising potential.

The AP for the samples in experiment A is totally controlled by pyrite and with this simple mineralogy S analyses (with correction for barite and chalcopyrite) provide an excellent estimate of the pyrite content. Thus all the analytical methods tested give the same AP (Figs. 4, 5, 6). In this case even the simple four-acid analytical data commonly available in mine databases provides an excellent indication of AP.

Figures 1 to 3. NP (CaCO₃ eq kg/t). X-axis = NP determined from combined qXRD and assay by weighted least squares method. **1)** Y-axis = predicted NP from linear programming with CO₂ and H₂O vs. Root mean squared

(RMS) difference of linear programming estimated from weighted least squared estimate 3.0; **2)** Y-axis = predicted NP from linear programming with LOI. RMS difference 9.3; **3)** Y-axis = predicted NP (CaCO$_3$ eq kg/t) from linear programming using limited assay data and no SiO$_2$. RMS difference 21.6;

Figures 4 to 6. AP (kg H$_2$SO$_4$/t)**.** X-axis = AP determined from preferred weighted least squared estimate. **4)** Y-axis = predicted AP from linear programming with CO$_2$ and H$_2$O. RMS difference 8.4; **5)** Y-axis = predicted AP from linear programming with LOI. RMS difference 7.6; **6**) Y-axis = predicted AP from linear programming using limited assay data and no SiO$_2$. RMS difference 7.5.
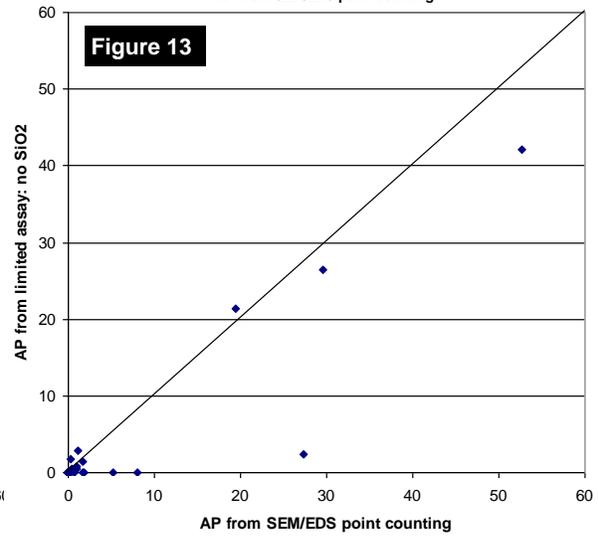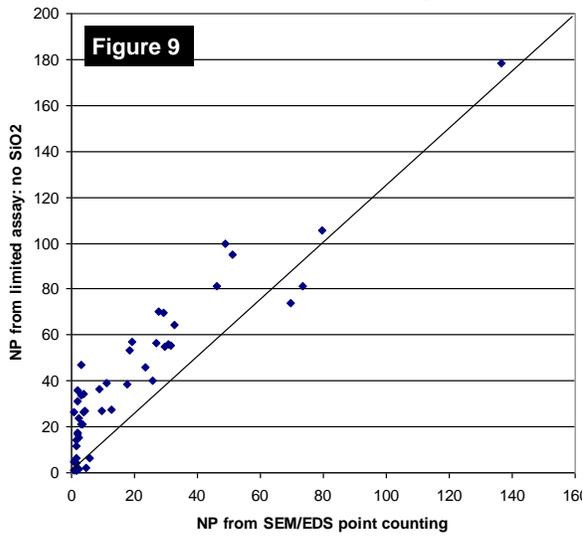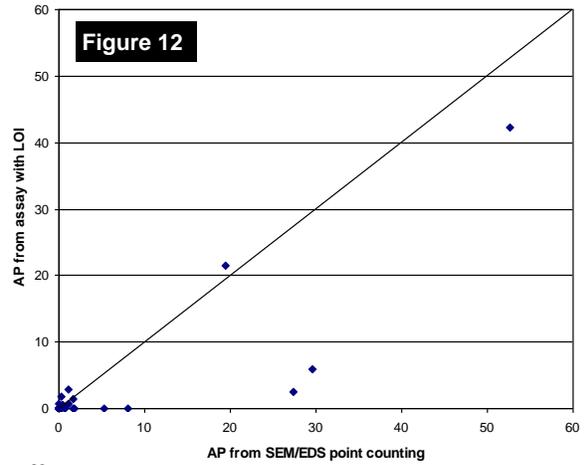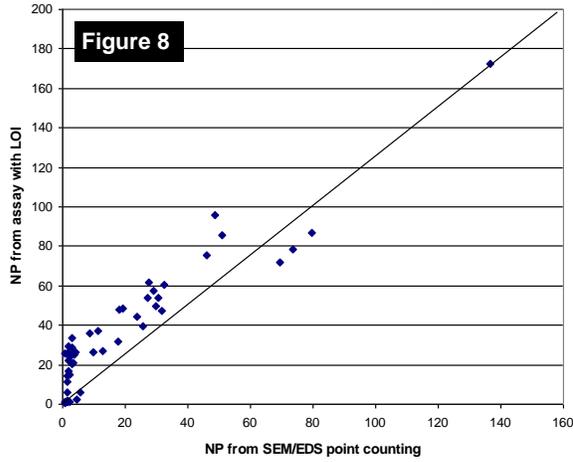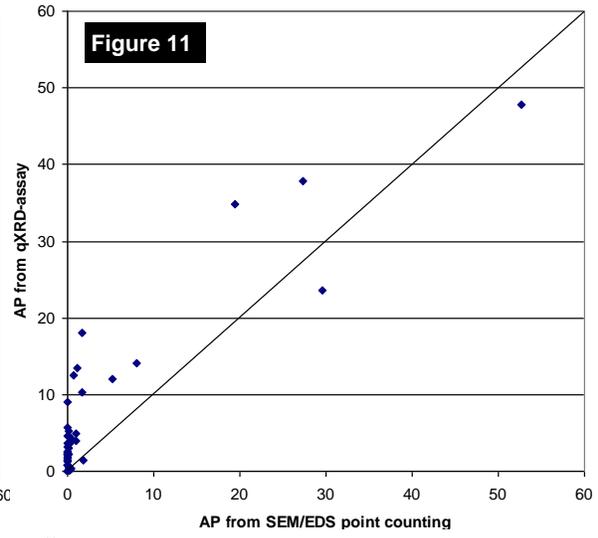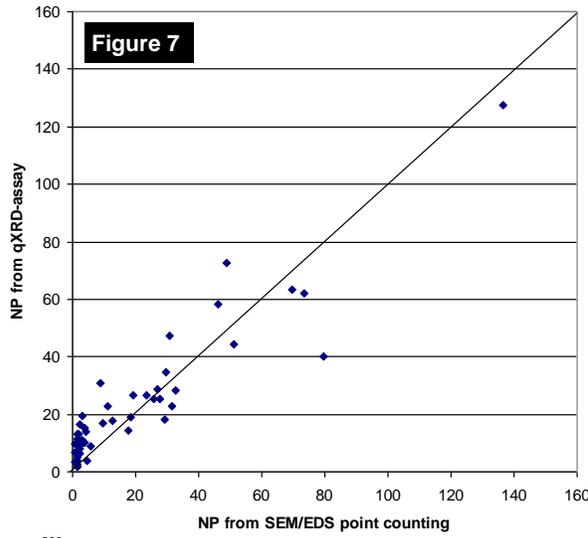
Experiment B: Complex assemblage

There are three different estimates of calculated mineralogy for the complex case. Using weighted least squares to combine qXRD and full major element assays by XRF gives an un-biased but not very accurate measure of NP. This can be seen by comparing the result with the more reliable SEM/EDS point counting method (Fig. 7). Using only analyses with LOI it is very difficult to balance the hydrous and carbonate minerals. In this example (Fig. 8), the NP was over-estimated by ~20 CaCO$_3$ eq kg/t at relatively low carbonate contents. With typical limited assay data (Fig. 9) the overestimate of the NP value was closer to ~30 CaCO$_3$ eq kg/t. These values suggest that, for the complex case in these experiments, the combined qXRD-assay method is required to adequately estimate NP. It is possible that a full assay (i.e. XRF + LOI) with CO$_2$ analysis would be sufficient but that was not tested on these rocks.
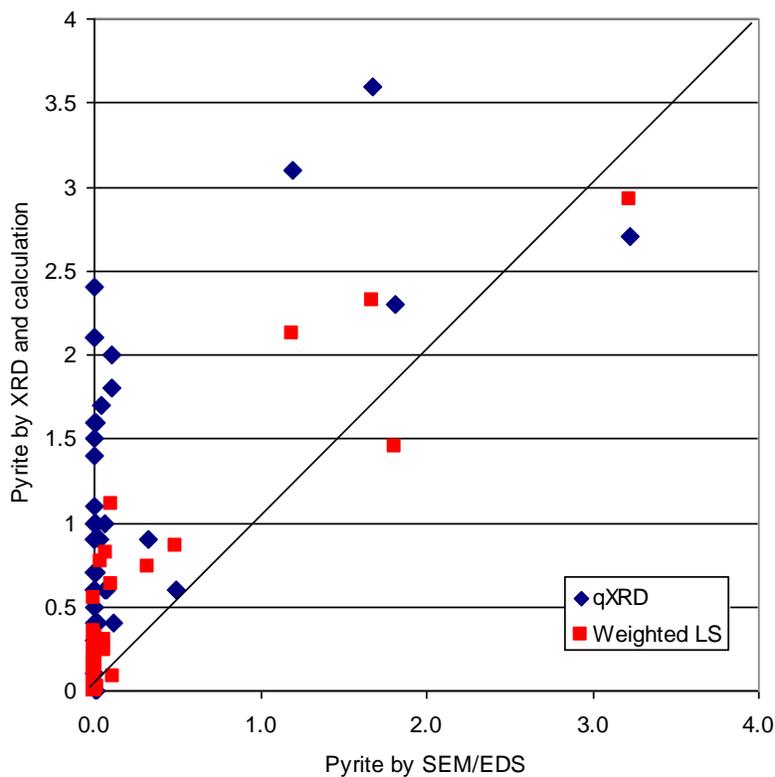
The qXRD analysis was strongly affected by the high X-ray fluorescence background in these high Fe rocks despite the use of a Co X-ray tube. The XRD laboratory noted that there was interference from an intense hematite XRD peak onto one of the main peaks of pyrite and they predicted that many of the low pyrite contents reported were too high. The combined qXRD-assay results inherit this bias to high pyrite estimates (Fig. 10). The comparison with the AP values determined from mineralogy based on SEM/EDS point counting suggests the pyrite content is overestimated by about 0.5%. This bias is seen as AP values that are about 10 kg H$_2$SO$_4$/t too high (Fig. 11) using the qXRD-assay estimates of mineralogy.

Using the assay data with LOI alone the AP values are generally too low (Fig. 12). With S allocated to four sulphides it is difficult to correctly predict the mixture on a routine basis. Most samples are close to the correct value but there are two outliers where the AP estimate is 20 kg H$_2$SO$_4$/t too low. The estimate based on a limited assay (Fig. 13) gives a similar result. While these methods are less robust than the qXRD-assay method they are not affected by the qXRD interference and have smaller average errors in AP value.

Figures 7 to 9 (below). NP (CaCO$_3$ eq kg/t). X-axis = NP determined from mineralogy based on SEM/EDS point counting. 7) Y-axis = predicted NP from weighted least squares integration of qXRD and assay data. RMS difference 10.6; 8) Y-axis = predicted NP from linear programming with LOI. RMS difference 20.9; 9) Y-axis = predicted NP from linear programming using limited assay data and no SiO$_2$. RMS difference 24.8.

Figures 11 to 13 (below). AP (kg H$_2$SO$_4$/t). X-axis = AP determined from mineralogy based on SEM/EDS point counting. 11) Y-axis = predicted AP weighted least squares integration of qXRD and assay data. RMS difference 5.4; 12) Y-axis = predicted AP from linear programming with assay data and LOI. RMS difference 5.3; 13) Y-axis = predicted AP from linear programming limited assay data and no SiO$_2$. RMS difference 4.1.

Figure 7

Figure 11

Figure 8

Figure 12

Figure 9

Figure 13

Figure 10. Comparison of pyrite estimates from qXRD alone (blue diamonds) and after merging qXRD with assay data using a weighted least squares method (red squares), with the more accurate estimate using SEM/EDS point counting.

CONCLUSION

Mineral grade calculated from assay data has potential to provide a low cost prediction of ARD potential, albeit, provided care is taken in the calibration and in selection of suitable assay characteristics. Quantitative (q)XRD is a robust method for identifying the major minerals in a sample. However the precision is poor and especially so at abundances less than 5%. Combining assay data with qXRD results leads to a substantially improved estimate of the mineralogy. Where there is an adequate training set of samples with "known" mineralogy, it is possible to estimate the mineralogy from assay data alone using linear programming.

In waste rocks with simple mineralogy it is possible to predict the ARD potential of rocks based on major element analyses where at least LOI is measured. However if the only available analysis are from four-acid assay data (no Si, no LOI) the NP cannot be accurately predicted and therefore the net acid production potential cannot be quantified.

Where the mineralogy is complex, with multiple S-bearing phases and/or mixed carbonates, ARD potential can be predicted from samples which have both qXRD and assay data. If only major element analyses with LOI are available the calculation of AP and NP are inaccurate and with only four-acid data no realistic estimate of ARD potential is possible.

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