An Novel Approach to Hydrogeochemical Risk Assessment Based on short-term tests

Francisco Ruiz Allén[1]

[1]Consultoría Geológica, S.L. (CONGEO), Real Oviedo 10, 33013 Oviedo, Spain, fruizallen@congeo.es

Abstract

An approach has been followed that attempts to obtain as much information as possible from the static tests. During the process some questions arise: the role of project site water analysis in a geochemical study, the inadequacy of standard ABA tests for estimating the effective neutralization potential of rock samples with silicates and little or no carbonates, the possibility of using the NAG test to help the geochemist to predict which lithologies release what, and to establish risk levels that help to define waste management and water treatment measures, before the results of long-term kinetic tests are available.

Keywords: Static testing, silicates, mineralogy, neutralization potential, NAG leaching.

Introduction

In Spain, it is not uncommon for environmental impact studies of metallic mines to be based on a set of geochemical tests consisting of ABA according to the European standard EN15875, rock analysis by aqua-regia and leaching test according to the European standard EN12457 (leaching test in deionised water for 24 hours). Mineralogical analysis of environmental samples is not included, and no account is taken of the additional information for the hydrogeochemical characterization that may be provided by actual site waters. Budgetary constraints, but above all the lack of involvement of a geochemist and the fear of misuse of the data by environmental groups may be part of the reasons.

A comprehensive set of geochemical static tests, together with site water data, has been used for the geochemical risk assessment of a lithium mine project located in northern Spain. In the project area there are old mining works of very small size. Lithium is found in pegmatites hosted in schists.

Of all the work done, the approach based on mineralogical estimation of the neutralization potential of silicates, which is considered challenging by several authors (Jambor 2006, Karlsson 2019, Morin 2007 and 2024), and the use of a risk index based on NAG eluates are discussed here. It also highlights the importance of verifying the NAG procedure followed by the laboratory and ensuring the complete oxidation of the samples.

Materials and Methods

The rock materials analyzed consisted of 24 drill core samples, 3 waste rock samples and 2 sediment samples. Drill core samples were dried at 60°C, crushed to below 2 mm and quartered to approximately 200 grams which were subjected to grinding to below 75 microns to obtain the subsamples required for the various analyses. In the case of the dump samples, the dry sample was previously sieved at 10 mm and at 2 mm for the sediment samples. The rest of the preparation was carried out on the finer fractions as indicated above.

Drill core samples were selected by the projects geologists based on dominant rock units and 3D spatial distribution. The position of the projected underground workings was considered, looking for the closest corresponding sample intervals in the drill-cores.

There is no seepage from the old waste dumps. Instead, there was information available of the quality of surface (streams) and ground waters (piezometers).

The selected geochemical tests were X-ray diffraction (XRD, Rietveld refinement method) mineralogy; ABA (acid-base accounting), using the European EN 15875 procedure; NAG (Net Acid Generation test) and leachability tests such as EN 12457, widely used for landfills, which would give immediate solubility or leachability, and the analysis of the eluate obtained in the NAG test, following the instructions of the AMIRA P387A Handbook (Smart *et al.*, 2002). Chemical analysis of the samples was carried out by extraction with aqua regia, a 3:1 mixture of hydrochloric acid and nitric acid, which is the most commonly used method in Spain for mine waste and soils pollution characterization. We think, however, that it would have been better to perform whole rock analysis to verify the mineralogical information and also to allow the application of the silicate neutralization model (Morin 2024).

The European standard for acid-base accounting – EN 15875 – requires reducing the size of the samples to less than 0.125 mm in 95% of particles. The final titration pH for the assessment of the Neutralization Potential (NP) is 8.3. Also, it differs from the Sobek and other modified methods in that it uses the carbonate content, calculated from the inorganic carbon, to assess the amount of hydrochloric acid to be used in the titration for measuring the NP, instead of using a Fizz test.

The single addition NAG test was used. The NAG method requires adjusting the pH at the beginning of the test between 4.5 and 6.0 by NaOH solution (AMIRA 2002, MEND 2009). This may give rise to a relevant inaccuracy in the test, as the pH obtained in the NAG test is compared with 4.5. For this reason, the laboratory was asked to regulate the pH as close to 4.5 as possible and to record that initial pH in addition to the NAG pH. Additionally, the eluates obtained in duplicates of the NAG test were analyzed to evaluate the release of sulfur and metals and to evaluate the complete oxidation of sulfides.

Results and Discussion

Acid-Base Accounting

Acid-base accounting (ABA) tests, either according to the American EPA 600 (Sobek) standard and its modifications, or the European standard EN15875, do not adequately reflect the solid-phase neutralization potential (NP) that silicates may have. This is because, in the short duration of the static laboratory tests, the silicates do not react – or react only to a limited extent – with the hydrochloric acid used (Morin 2024). This is a key issue, as lag times to the onset of acidity are usually calculated from the total NP and AP derived from the ABA standard and their depletion in humidity cell tests (HCT).

Inspired by the work of Karlsson *et al.* (2019), an approach following Kwong (1993), rather than Lawrence and Scheske (1997), was attempted here. Interestingly, both approaches use data from Sverdrup (1990), but Lawrence and Scheske assign an order of magnitude less reactivity to intermediate weathering silicates than Kwong. XRD mineral concentrations were converted to moles/kg according to their ideal formula molecular weight, and then to moles of H+ using the Kwong formula according to Sverdrup. The results were converted to moles of $CaCO_3$ equivalent (1 mol $CaCO_3$ equivalent = 2 mol aqueous H+, pH < 6.3) and then to kg $CaCO_3$/t.

Similarly, Jambor *et al.* (2006) have proposed their own mineral-specific NP values, based on performing the Sobek procedure on freshly prepared monomineralic samples of some minerals, but using a protocol to standardize the time and temperature of the acidification step in the Sobek method. The NPs according to Jambor *et al.* were assigned to the minerals, the NP of the whole sample was obtained by addition of the NPs according to the weight content of the different silicate minerals in the sample.

Lawrence and Scheske state that the Sobek test may overestimate NP availability under real field conditions for many samples. Also, Jambor *et al.* show that NP results for most plagioclase series increase linearly with increasing Ca in the formula. Both statements are contrary to the NP model presented by Morin (2024), according to which Sobek usually underestimates the NP of plagioclase silicates, and plagioclase reactivities increase exponentially with Ca content (which is also shown in the data used by Kwong and Lawrence and Scheske).

The NPs calculated after Kwong show consistently higher values than those obtained by EN 15875 (Fig. 1), even when quartz has been assigned 0 and not 0.004 as reactivity. The NPs calculated according to Jambor are very low, presumably because quartz varies between 35 and 58% in the schist samples, and between 21 and 32% in the pegmatites. Other minerals present are muscovite, biotite, K-feldspar and albite, all of which are assigned 1 after Jambor, except for quartz (0) and biotite (which is assigned 8 as phlogopite). Jambor NPs are based on the Sobek procedure (granulometry 0.250 mm, acid digestion at 85°C, titration pH at 7.0), whilst EN 15875 is done on <0.125 mm sample, 24 h at room temperature, titration pH at 8.3).

All these approaches used in this work have shown some drawbacks. First, the actual effective NP in samples with silicates cannot be known from static tests. The rate of oxidation of sulfides and the amount of sulfides present are critical. This is largely a site-specific and kinetically determined parameter. So, there is no reference to compare with. Second, there are some minerals not considered in the mentioned publications so, when there were no data, the assignment of reactivities was based on similarities in the mineral formula, considering the presence of Ca and Mg mainly. Third, the results differed between mineralogical approaches (Fig. 1). Four, XRD proved to be blind to the different plagioclases present, which were reported generically as albite. Analysis of rocks with aqua-regia, showed that Ca was present up to 0.56% in the schists samples. Unfortunately, digestion with aqua-regia provides limited dissolution of the silicates, depending also on the mineralogy. Whole-rock analysis should have been used instead to verify the calcium concentration. The ongoing HCTs on two samples are showing that Ca is the main cation released on a molar basis. Therefore, it is very likely that Ca plagioclase is present in the samples. Calcium molar ratios using SEM/EDX should have been carried out (Morin 2024).

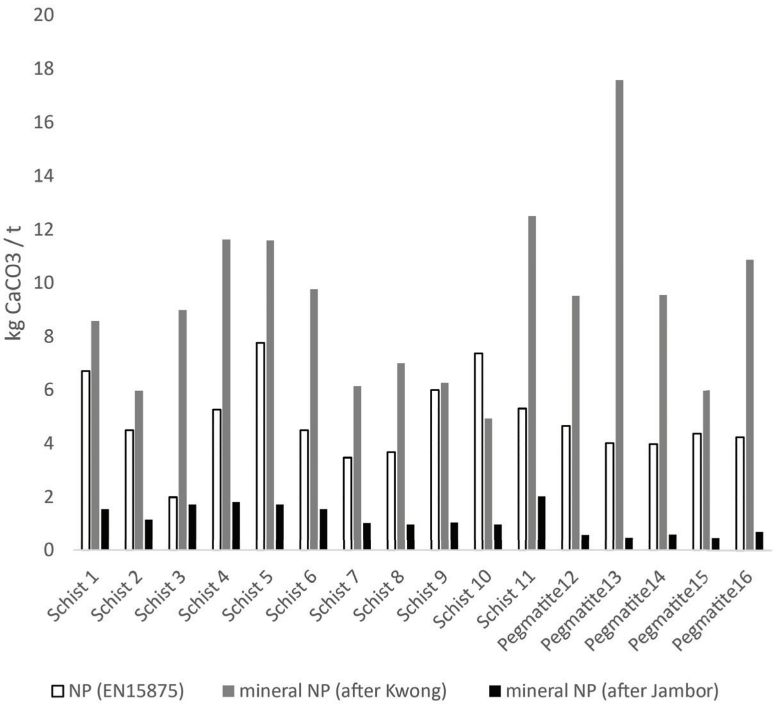

Figure 1 *Neutralization potentials of samples from the mine project.*

Leaching tests

The "Manual for risk assessment of closed or abandoned extractive industries" (IGME, 2014), among other tests to assess the risk in former mine dumps, calculates a mean hazard quotient (CPPlab) from the leachability test following the EN 12457 standard on waste dump samples. This test consists of putting 90 g of the material, crushed to less than 10 mm, in contact with 900 ml of deionized water. The mixture is stirred for 24 hours and filtered at 0.45 mm for analysis.

The average hazard quotient is calculated from the relationships between the concentrations in the leachate and the Spanish environmental quality standards (EQS) for the protection of the aquatic environment, which are derived from the European Water Framework Directive and are the same in several European countries.

$$\mathrm{CPP_{LAB}} = \frac{1}{\mathrm{n}}\sum^{n}\frac{[X]_{LIX-LAB}}{NCA_X} \qquad \text{(IGME 2014)}$$

Where $[\mathrm{X}]_{\mathrm{LIX\text{-}LAB}}$ is the concentration measured in the leachate resulting from applying the EN 12457–2 laboratory procedure to the waste for element X; NCAX is the target concentration in the receiving watercourse corresponding to element X; and n is the number of elements for which the concentration measured in the eluate is higher than the value adopted as a standard.

On the other hand, the Gard Guide (INAP, 2009) presents the Geochemical Abundance Index (GAI) as an indication of elemental enrichment. The GAI for an element is calculated as follows:

$$\mathrm{GAI} = \log_2\left[\frac{\mathrm{C}}{1.5\times \mathrm{S}}\right] \qquad \text{(INAP 2009)}$$

where C is the concentration of the element in the sample and S is the median content for that element (mean world soil, crustal abundance, etc). A GAI of 0 indicates that the element is present at a concentration similar to, or less than, median abundance and a GAI of 6 indicates approximately a 100-fold, or greater, enrichment above median abundance (INAP, 2009).

The drawback of the GAI is that it is not related to the mobility of metals and hence, it does not really give any indication of the elements that may actually affect the water quality in a future mining project.

Recognizing the shortcomings of the GAI identified above, an index has been developed using a formulation analogous to that of the GAI but applied to NAG test eluates.

$$NagI = \log_2\left[\frac{C}{1.5\times EQSx}\right]$$

Where, C is the concentration of the parameter in the NAG eluate and EQSx, as in the IGME procedure applicable to EN 12457, the Environmental Quality Standard, i.e. the maximum allowable or target concentration in the receiving watercourse corresponding to parameter X. In this case, a NagI of 3 represents 12 to 24 times the water quality target.

Another logarithmic formula was previously tried, but the sensitivity was not enough for the work. Using the following formula, a NagI of 3 represents 250 to 1250 times the water quality target concentration and table 1 showed no numbers except for Cu in some samples.

$$I = \log_5\left[\frac{C}{2\times EQSx}\right]$$

The sulfate concentrations in the NAG eluates were compared with those of the mining-influenced waters at the site as a reference for possible upscaling between the laboratory and the field. This also helped to choose the first logarithmic formula as the appropriate one. Also, the site water analyses and the mineralogy were used to verify that no parameters are missing in the levels of risk identified in the NAG eluates. The influence of elements that may be volatilised under the NAG test conditions (which requires heating on a hot plate), such as mercury and its compounds, has not been evaluated.

At the mine project, after comparison with EQS, the elements that had been found to be relevant in the groundwater analyses were Cu and Zn in some borehole water samples. Using the approach proposed here, in addition to Al and Fe, Cu and Zn appear as elements of concern in the NAG eluates of the analyzed rock samples (Table 1). The pHs obtained in the NAG eluates do not suggest that significant metal precipitation may have occurred, except for aluminum

Table 2 Risk indexes calculated from NAG eluates for the mine project.

			pH –	pH –	F mg/L	Sulfate mg/L	Al µg/L	Sb µg/L	As µg/L	B µg/L	Cd µg/L	Co µg/L	Cu µg/L	Cr µg/L	Fe µg/L	Mn µg/L	Hg µg/L	Mo µg/L	Ni µg/L	Pb µg/L	Se µg/L	U µg/L	Zn µg/L
Sample	**Lithology**	**Depth (m)**	**NAG**	**NAG eluat**	**1,7**	**250**	**200**	**10**	**50**	**1500**	**0,45**	**20**	**5**	**50**	**200**	**50**	**0,07**	**70**	**35**	**14**	**1**	**30**	**30**
1	Schist	29	5,35	4,62	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2	Schist	41	6,47	4,97	–	–	1	–	–	–	–	–	1	–	–	–	–	–	–	–	–	–	–
3	Schist	16	5,27	4,76	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4	Schist	25	5,60	4,37	–	–	1	–	–	–	–	–	3	–	–	–	–	–	–	1	–	–	–
5	Schist	178	4,62	3,98	–	–	1	–	–	–	–	–	3	–	1	–	–	–	–	–	–	–	–
6	Schist	8	4,95	4,38	–	–	1	–	–	–	–	–	1	–	–	–	–	–	–	–	–	–	–
7	Schist	15	5,33	4,25	–	–	2	–	–	–	–	–	3	–	1	–	–	–	–	–	–	–	2
8	Schist	255	5,93	4,53	–	–	1	–	–	–	–	–	2	–	1	1	–	–	–	–	–	–	1
9	Schist	275	5,78	4,25	–	–	1	–	–	–	–	–	3	–	1	–	–	–	–	–	–	–	–
10	Schist	12	5,04	4,49	–	–	1	–	–	–	–	–	1	–	1	–	–	–	–	–	–	–	–
11	Schist	43	5,59	4,45	–	–	1	–	–	–	–	–	2	–	1	–	–	–	–	–	–	–	1
12	Schist	55	5,56	4,62	–	–	1	–	–	–	–	–	2	–	1	–	–	–	–	–	–	–	–
13	Schist	108	5,82	4,41	–	–	1	–	–	–	–	–	2	–	1	–	–	–	–	–	–	–	–
14	Schist	249	6,22	4,52	–	–	1	–	–	–	–	–	3	–	1	–	–	–	–	–	–	–	–
15	Pegmatite	78	5,10	4,50	–	–	2	–	–	–	–	–	1	–	–	–	–	–	–	–	–	–	2
16	Pegmatite	57	5,08	4,62	–	–	2	–	–	–	–	–	2	–	–	–	–	–	–	–	–	–	2
17	Pegmatite	299	5,91	4,71	–	–	2	–	–	–	–	–	1	–	–	1	–	–	–	–	–	–	–
18	Pegmatite	196	5,78	4,76	–	–	2	–	–	–	–	–	1	–	1	2	–	–	–	–	–	–	1
19	Pegmatite	156	4,98	4,84	–	–	2	–	–	–	–	–	2	–	–	–	–	–	–	–	–	–	–

and iron, which would explain the observed drift in pH between the NAG assay for the ABA classification, and the duplicate for the analysis of the NAG eluates, which is assayed one day later. This precipitation of Al and Fe could potentially result in losses from solution by adsorption or co-precipitation of some metals, e.g. arsenic, but no arsenic was found in the site waters above D.L. nor arsenopyrite in the deposit.

Conclusions

This study investigated the possibility of using an XRD mineralogy neutralization potential (NP) based on Kwong (1993), comparing also with Jambor (2006) as a preliminary approach to verify the NP obtained by standard ABA methods. However, the results were very different and actual effective NP remains unknown. Also, XRD proved to be blind to the different plagioclases that may be present, which were reported as albite. However, ongoing HCT has shown that the main cation released is Ca. Nevertheless, the NP values were higher than those obtained by EN15875, and this may be useful to check whether silicate neutralization is being underestimated in the ABA assay. An approach such as the model suggested by Morin (2024) is likely to be much more accurate. It requires the use of SEM-EDX to identify Ca content on selected silicate mineral particles, which was not carried out in this study.

Along with mineralogy, site water analyses are considered essential for a comprehensive approach and very useful as a reference or to calibrate risk assessment models. Test procedures should be carefully checked in continuous communication with the analytical laboratory. This is especially relevant with the NAG procedure. The recommendation to use a multiple addition test has been confirmed, even for samples with low sulfide content (Parbhakar-Fox 2018). In addition, for the initial hydrogen peroxide solution, the NAG procedure states: “Aim for a pH of 4.5 and no higher than 6.0” AMIRA Manual P387A (Smart *et al.*, 2002). We recommend asking the laboratory to bring it as close to 4.5 as possible.

The application of an index based on the comparison of element concentrations in NAG eluates with the Environmental Quality Standards for water, is considered very promising as a tool to identify which lithologies release what, at what level of risk, and to design waste management measures, on a risk-based approach rather than on water quality prediction.

Acknowledgements

The author thanks the mining company for participating in these investigations and for facilitating the necessary field work. Special thanks to Dr. Kevin A. Morin, Mine Drainage Assessment Group, for his expertise, open publications and technical discussions over the recent years.

References

Alberruche ME (2014). Manual for risk assessment of closed or abandoned extractive industries [Manual para la evaluación de riesgos de instalaciones de residuos mineros cerradas o abandonadas]. Instituto Geológico y Minero de España (IGME)

Jambor JL, Dutrizac JE, Raudsepp M (2006) Comparison of measured and mineralogically predicted values of the Sobek neutralization potential for intrusive rocks. 7th International Conference on Acid Rock Drainage (ICARD), March 26–30, 2006. American Society of Mining and Reclamation (ASMR).

Karlsson T, Räisänen M L, Lehtonen M, Alakangas L (2019) Comparison of static and mineralogical ARD prediction methods in the Nordic environment. Environmental Monitoring and Assessment 190:719.

Kwong J (1993) Prediction and Prevention of Acid Rock Drainage from a Geological and Mineralogical Perspective. MEND Project 1.32.1. Canmet, Ottawa, Canada.

Lawrence R, Scheske M (1997) A method to calculate the neutralization potential of Mining wastes. Environmental Geology 32 (2) September 1997 7 Q Springer-Verlag.

Morin KA (2024). Silicate Neutralization Potential Focussing on Plagioclase, and the MDAG Silicate NP Model. MDAG Internet Case Study #80.

Morin KA, Leroux J, Lamontagne A, Michaud ML, Dy E, Huang C (2024). Predictions of ARD Potential Dominated by Silicate Neutralization Potential at the Troilus Gold Minesite, Québec, Canada. ICARD 2024.

Parbhakar-Fox A, Fox N, Ferguson T, Hill R, Maynard B (2018) Dissection of the NAG pH Test: Tracking Efficacy Through Examining Reaction Products. IMWA proceedings 2018.

Smart *et al.* (2002) ARD Test Handbook Project P387A, Prediction and Kinetic Control of Acid Mine Drainage. AMIRA International, Melbourne.

The International Network for Acid Prevention (INAP), 2009. Global Acid Rock Drainage Guide (GARD Guide).