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Characterization of waste — Kinetic testing for assessing acid generation potential of sulfidic waste from extractive industries

National foreword

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Characterization of waste - Kinetic testing for assessing acid generation potential of sulfidic waste from extractive industries

Caractérisation des déchets - Essais cinétiques pour la détermination du potentiel de génération d'acide des déchets sulfurés des industries extractives

Charakterisierung von Abfällen - Kinetische Prüfungen zur Bestimmung des Säurebildungspotentials von sulfidhaltigen Abfällen der mineralgewinnenden Industrie

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Foreword

This document (CEN/TR 16363:2012) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

The preparation of this document by CEN is based on a mandate by the European Commission (Mandate M/395), which assigned the development of standards on the characterization of waste from extractive industries.

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Introduction

A specific feature of sulfide containing waste is the risk for acid/neutral drainage generation (A/NRD). Acid drainage occurs if the acid generation from sulfide oxidation exceeds the acid buffering from minerals in the waste while, in this context, neutral drainage occurs when neutralisation generation exceeds the acid generation.

Test methods for the determination of acid generation behaviour can be divided into static and kinetic tests. A static test is used for screening purposes. It is usually relatively fast to perform, but gives only indicative information based on total content of sulfur (or sulfides) and of readily available buffering minerals in the waste material. Kinetic tests give more detailed information on behaviour based on the determination of mineral reaction rates under specified conditions. A European Standard, EN 15875, has been established for the static testing, while this Technical Report gives guidance on how the kinetic testing may be performed and interpreted.

Kinetic testing has been required as part of permit processes for many new and operating mine sites. Many different test methods have been used over the last 20 to 30 years. These tests are commonly designed to avoid that the oxidation rate is limited due to the lack of oxygen or build-up of secondary minerals. Kinetic tests based on current standards and laboratory-scale standard practise (ASTM D5744 - 96:2001 and ASTM D5744 - 07:2007; Morin and Hutt, 1997; Lapakko, 2003) are not designed to evaluate short- and long-term drainage water quality. However, adjustments to the standard protocols can be done to produce indicative information about short-term drainage water quality. Together with modelling, this information can be used to predict/estimate long-term drainage water quality.

This Technical Report is a guidance document that discusses the main kinetic test methods that are used within the mining sector internationally, the applicability of the different tests and how to evaluate the results. Kinetic test results may provide valuable information, but it is important to understand their limitations. Sulfide oxidation in the field is controlled by many different factors that may be difficult to simulate within the laboratory. Some of these factors may in fact be unknown at the time of testing. The complexity of applying test results to field conditions may to some extent be balanced by long experience in evaluating such data.

The objective of this Technical Report is to support the management of waste from extractive industries by giving guidance on how to characterize the kinetically controlled process of acid drainage generation.

The target audience of the document includes all stakeholders concerned with the management of extractive waste including the extractive industry, authorities, regulators, consultants, and testing laboratories.

Document structure

This Technical Report is organized to provide the answers to the three main questions below.

What type of data will kinetic testing provide and what methods are available? Clause 2 Methods	After introducing the concepts of kinetic testing for assessing acid generation potential of sulfidic waste, this clause (Clause 2) describes what type of information these tests provide. This clause also reviews the different tests methods and the ability to meet the objectives set out for the different kinetic tests. Methods to evaluate both acid generating reactions and neutralizing reactions are described.
How can the data be interpreted? Clause 3 Interpretation and evaluation	This clause (Clause 3) gives guidance on how results from kinetic tests can be applied. Included in this clause is guidance on how results from the tests may be used to calculate the bulk oxidation rate for the material; to evaluate the leaching rates for elements within the test system; and based on the results, to evaluate mineral reactions in the system. Kinetic test relevance for describing field scale processes is discussed.

What method to select? *Clause 4 Recommendations*	The clause ends with recommendations on the selection of kinetic test design depending on objective(s).

1 Scope

This Technical Report describes the performance and evaluation of kinetic tests for sulfidic waste material that, according to previous testing (primarily acid base accounting), is likely to go acidic or when the result of such testing is inconclusive. This Technical Report also covers the issue of drainage from sulfidic material that is likely to be well buffered but that will produce a neutral drainage potentially affected by sulfide mineral oxidation.

This Technical Report will not include aspects of sampling and testing that are already covered in the overall guidance document for characterisation of extractive waste (CEN/TR 16376) or in the guidance document on sampling of wastes from extractive industries (CEN/TR 16365).

2 Methods

2.1 General

It is necessary to have a good understanding of the waste material before kinetic (mineral reaction rate) testing is performed. This together with well-defined objectives will aid in selecting the methods. This clause describes the planning of kinetic testing, key elements to analyse for, and the main methods used by the industry.

2.2 Planning

Figure 1 shows a flow chart of the different steps to consider when planning for kinetic testing. A number of the steps in the flow chart are not further discussed in this document. More details on topics related to sampling are found in CEN/TR 16365, e.g. supporting information, data quality, documentation and reporting are discussed in overall guidance document (CEN/TR 16376). Additional information that puts kinetic testing in a wider context may also be found in the overall guidance document.

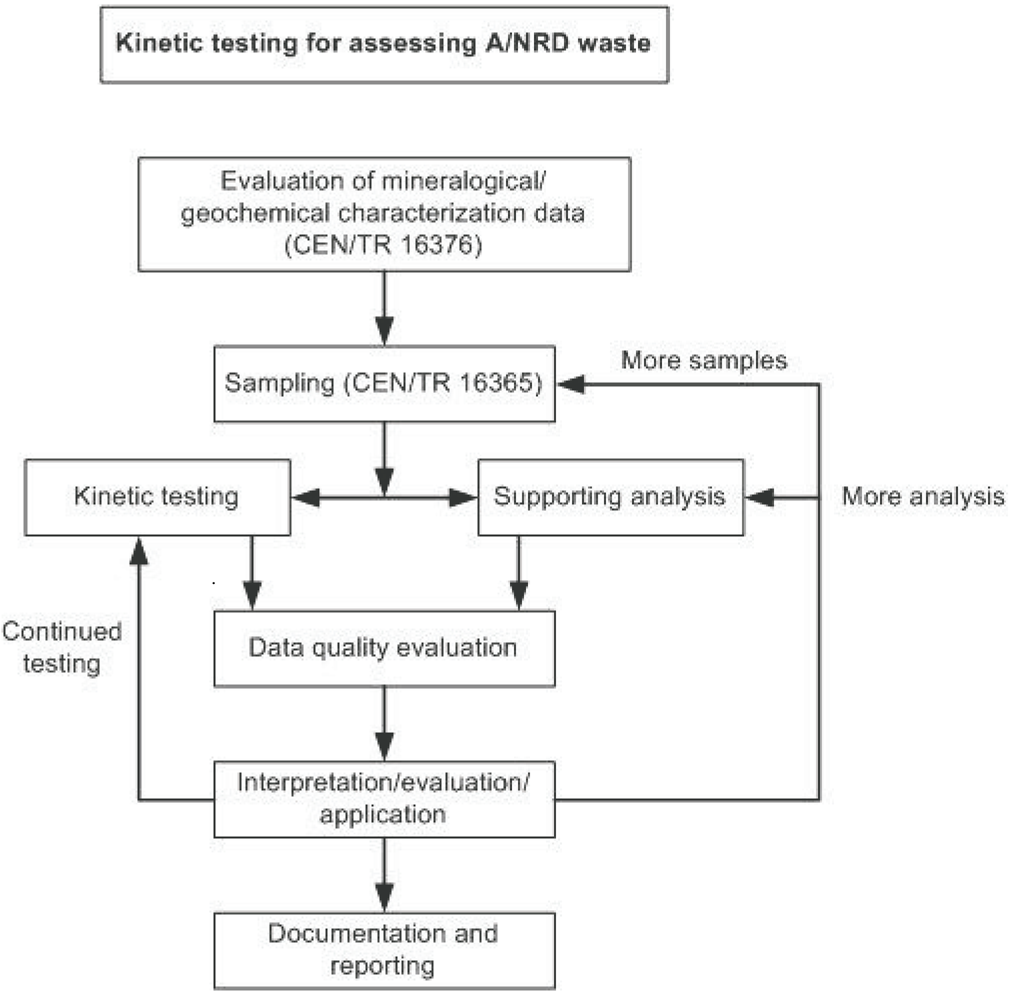

Figure 1 — General outline of the steps involved when performing kinetic testing for assessing acid/neutral generation potential of sulfidic waste from extractive industries

The only kinetic test method that has been standardized is the so-called humidity cell test (HCT) (ASTM D5744 - 96:2001, ASTM D5744 - 07:2007 and ASTM D5744-12; Sobek et al, 1978). This method has been used extensively in the mining sector. The method is designed to evaluate long-term acid generation potential and not to predict long term mineral reactions and mineral leaching in the actual tailings management facility (TMF) or waste rock dump, as pointed out by Sobek et al (1978) and re-emphasized by Lapakko et al (2003) and EIPPCB (2004).

Kinetic tests can be designed as small laboratory tests or large-scale field tests. During the exploration phase only smaller amounts of material are available and humidity cell test are the most common kinetic test used. The interpretation of the humidity cell test may help in defining feasible waste management options.

Most of the laboratory tests are run with relatively small amounts of crushed material (a few hundred grams to a few kilograms) with an optimal amount of oxygen available. The amount of rinse solution used is intended to be high enough to ensure removal of all reaction products, so that secondary precipitates do not limit reactions. However, at higher pH (> 4 to 5) iron oxides are likely to precipitate.

If the exploration project proceeds into mining, larger amounts of material will become available for testing. This may give the opportunity to design and run tests that are larger and/or more suited to site-specific conditions (column tests, lysimeter tests, field tests, etc.). These tests will give more reliable results for evaluating the long-term oxidation and leaching rates.

Kinetic testing may be performed several times through the lifetime of an extractive operation. It is common to establish field tests with extensive instrumentation at an early stage of operation. These field tests can be considered kinetic verification tests and will give valuable information for the final planning for closure.

In summary, the main kinetic tests designs used by extractive industries internationally are:

- humidity cell tests;
- column tests;
- lysimeter tests; and
- field tests.

The humidity cell has a standard protocol while the other methods are site specific and not standardized. In practise, also the humidity cell test that are being run are for or by the extractive industry commonly deviate from the standard design by introducing more site-specific aspects.

If the humidity cell protocols are followed, the reaction products are to be flushed out at cyclic intervals. Column experiments can, however, be designed to allow for build-up of secondary minerals by reducing the water amount for flushing. The column is likely to induce a concentration gradient along the length of the axis in the flow direction.

There are also other test methods that can be useful for testing certain processes and reaction rates under given conditions. The listed four most commonly used tests are described in the following sections complemented by a few additional tests that may be useful for evaluating reaction and leaching rates.

2.3 Testing data

The kinetic testing data to be obtained from the different tests will depend on the defined objective(s). The primary data commonly include pH, alkalinity, sulfate and weight of the sample. However, when analysing leachate samples, it is often beneficial for the understanding of the processes within the tested material to do a multi-element analysis. Kinetic testing requires collecting and analysing many samples over a long period of time (months to years). Only a few basic parameters are normally analysed on a regular basis. When there is a significant change in the basic parameters (e.g. pH and sulfate, see below), a full chemical analysis of the leachate may be performed to better understand the processes taking place and to provide input data for estimations/evaluations of drainage water quality.

The key parameters will commonly include:

- alkalinity;
- pH;
- sulfate;
- total dissolved solids;
- key metals (copper for copper mines, nickel for nickel mines, etc.); and
- element concentrations (anions and cations) in the leachate.

In order to understand the geochemical processes taking place within the tests columns information may also be needed on test conditions and on the tested material. Relevant information may include:

- flow rate of air and water;
- oxygen / carbon dioxide (during the test run, under sealed conditions);

- temperature (during the test run);
- mineralogy/speciation (before and after testing);
- speciation/element availability (before and after testing) and;
- grain size or surface area evaluation (before testing).

The data is commonly plotted in time versus concentration or accumulated concentrations (Figure 2). These types of plots help in understanding the processes taking place within the testing material, under the given conditions of the tests.

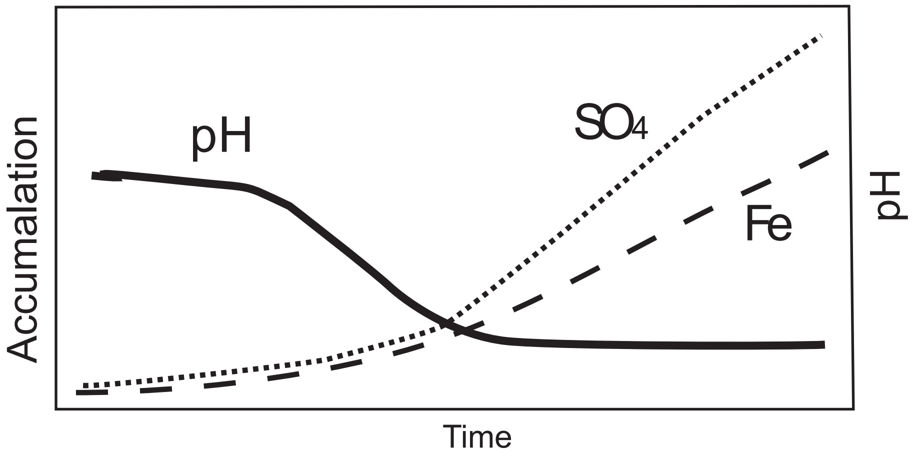

Figure 2 — Time versus pH and cumulative concentrations of iron and sulfate

2.4 Humidity cell test

In the late 1960s, kinetic tests were defined to evaluate and predict acid drainage from coal wastes (Caruccio, 1968), then called humidity cell tests. However, the method that has been most commonly used is the method designed by Sobek et al (1978) called simulated weathering cells, also referred to as humidity cell tests. This test setup has been modified to be more applicable for waste rock material and larger samples. The original method used 200 g material crushed to less than 2 mm placed in a “shoe box” container; while the later setup (ASTM D5744 - 96, 1996 and 2001, and ASTM D5744 - 07:2007) suggests using a 1 kg to 2 kg sample crushed to less than 6,5 mm grain size in a column rather than a shoe box.

The humidity cell test is designed to:

- determine if the material can go acidic or not; and
- assess the rate of oxidation under laboratory conditions.

The tests are commonly performed using 2 kg to 5 kg crushed material (< 6 mm). The material is placed in a column with a lid. Air is pumped through the column. The original procedure specifies alternating dry air-humid air, three days each while Price (2009) and EPA method 1627 (2009) recommends using only humid air. EPA method 1627 also recommends adding 10 % CO_2 to the humid air. Once a week, the sample is rinsed with a specific volume of water and drained. The collected water is measured and analysed for parameters as listed above (2.3). The tests are commonly run for at least 20 weeks, but in many cases up to a year or more.

The size of the columns may vary depending on the type of material used. Figure 3 shows a typical column test setup based on the concepts of the humidity cell test (ASTM D5744 - 96:2001 and ASTM D5744 - 07:2007; Price, 2009).

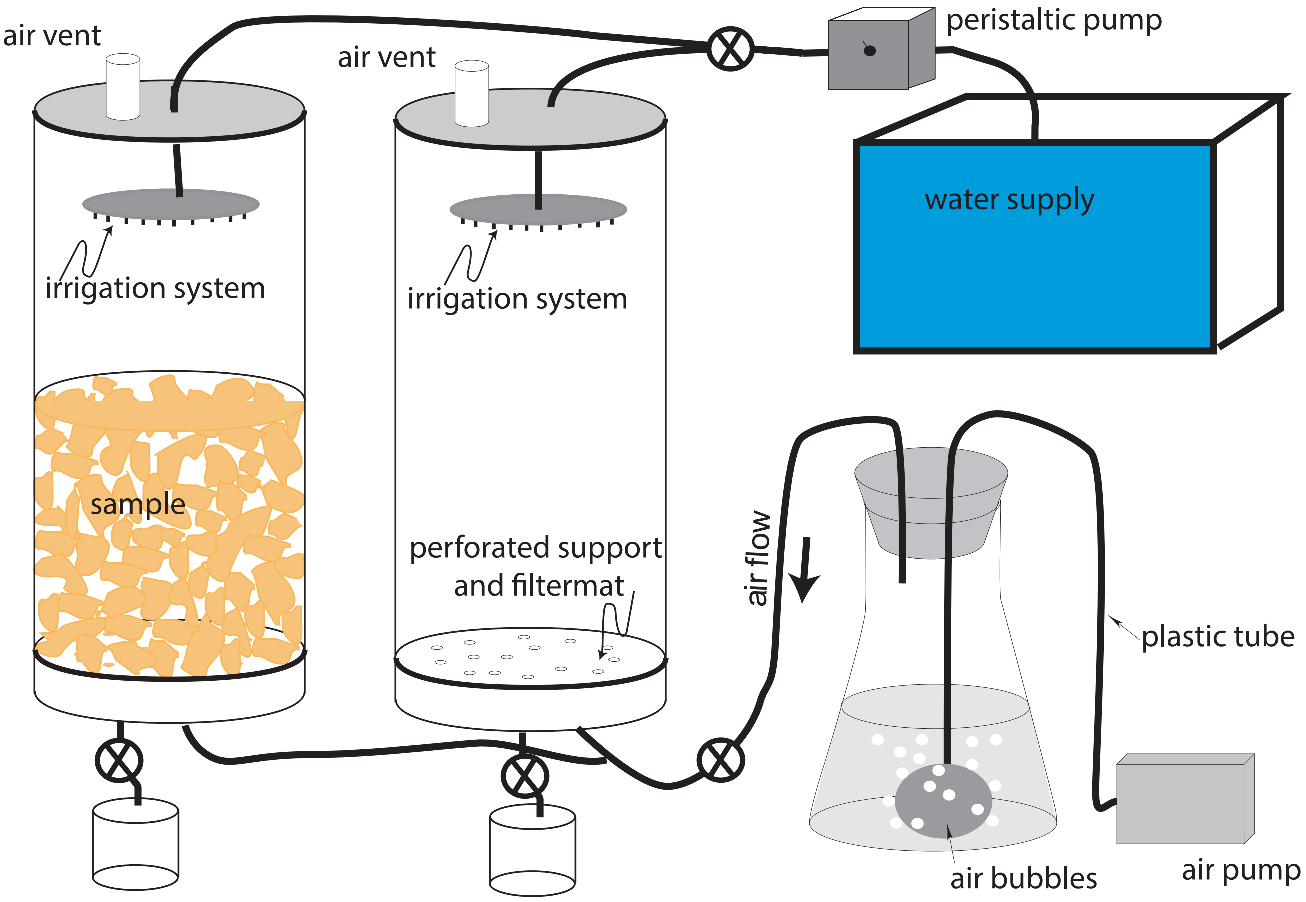

Figure 3 — Illustration of a common setup for humidity cell test for waste rocks and coarser tailings material (from Walder and Schuster, 2003) based on a standard method (ASTM, 2001, 2007). Column is commonly 10 cm to 20 cm in diameter and 20 cm to 40 cm high

The column tests with air flowing through and water rinsing through the material to leach the secondary products once a week for analysis, are not suited for finer grained material with low hydraulic conductivity (see Clause 3 for further discussion on this issue).

2.5 Other column tests

Column tests, other than the humidity cell test, are designed for site-specific use and are, therefore, not standardized. They can simulate a natural system to a much greater extent than any of the other laboratory scale kinetic test methods. The columns can be set up so that a solution, either recirculation or primary, flows through a column of crushed rock or milled material. The material can be fully or partially submerged. The flow rate of the solution can be adjusted.

Site-specific conditions included in the test design may be e.g. (Figure 4):

— Tailings may be deposited under water and, therefore, a column with submerged material may give valuable information. Water current may be introduced in the column to simulate natural conditions (prSN/TR 9432). Data from columns where waste material is sub-merged in water may be evaluated in combination with data from standard humidity cell tests.

— Covers considered as a closure option may be tested in a column with fresh material or material that has reached a steady state release rate, however, this requires full control of oxygen transport (sealed columns) in order to avoid misleading data to be generated.

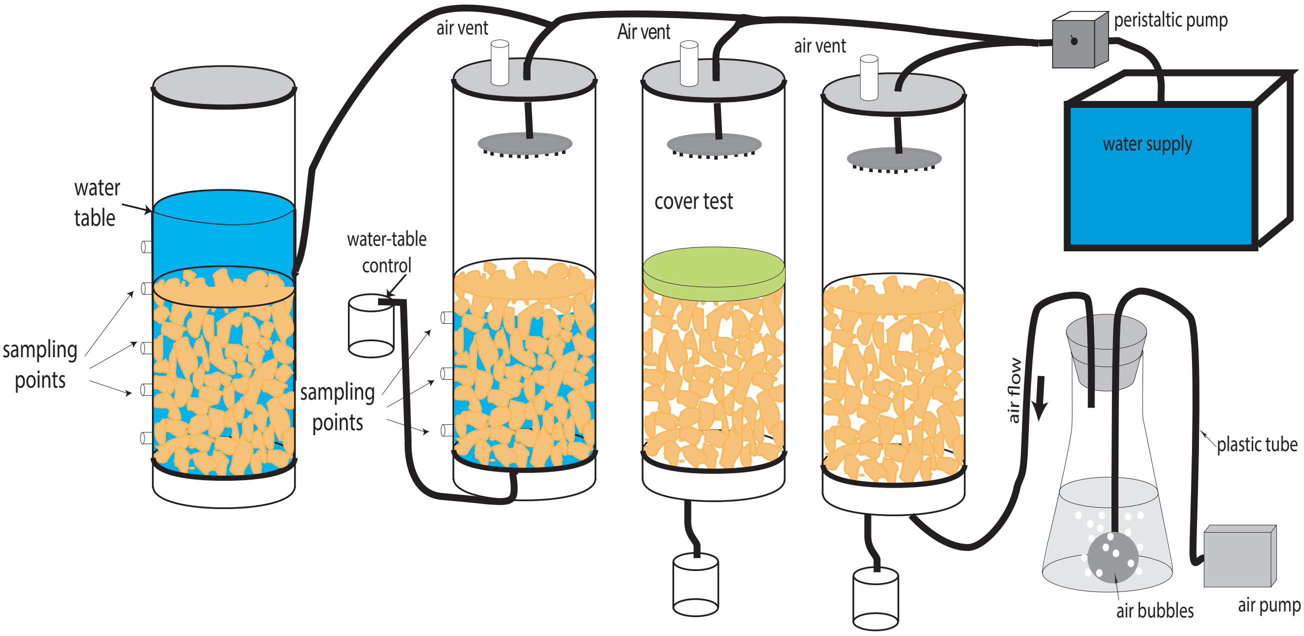

Figure 4 — Illustration of a selection designs for column test for waste rocks/tailings material. The column dimensions are site specific. The right column is a control and the other three are showing different management scenarios. The control of the water level can be set up in different ways depending on the objective of the investigation

Water monitoring, sampling, and analysis within the column should be designed for the specific needs of the site/objectives of the tests. These may be:

- water samples at different depth;
- humidity measurements under a cover;
- dissolved oxygen measurements in the submerged tailings; or
- O_2 / CO_2 measurements below the cover.

2.6 Lysimeter

The lysimeter test is an important bridge between laboratory scale tests and large scale field tests. A lysimeter is a device for collecting water from the pore spaces of soils for determining the soluble constituents removed in the drainage (EIPPCB, 2004) and to evaluate flow and infiltration rates. It may be a stand-alone test system or combined with other tests and analysis.

Lysimeters are normally used for soil research, but can be used for other permeable material, such as mine waste material. There is no standardized practice or design. Usually, mining waste lysimeters have a large diameter compared to the height, and are more voluminous than columns (may be several meters in diameter and height). They are normally used outdoors. Lysimeters are able to simulate field conditions scaled up from the laboratory experiments. The main drawback is long test duration. To capture matrix-macro flow issues within waste rock dumps Smith and Beckie (2003) recommend having lysimeter sizes of at least 4 m x 4 m.

2.7 Field test

2.7.1 General

The main purpose of field tests is to scale up laboratory tests to better reflect site climatic conditions and actual particle size distributions. Field tests may also be used to evaluate mitigation options, such as mixing of different waste materials or the performance of different cover designs, or to perform in-field leach tests.

At existing mines, field tests may be the most applicable test method to use for prediction of acid generation and metal leaching, while the possibility for field tests is limited during exploration. Field tests include:

- rainfall simulation leach tests performed in the field;
- pilot scale tests set under field conditions in a controlled environment;
- collection of seeps from confined waste material; and
- waste dump design with instrumentation.

Rainfall simulation tests and large-scale column/dump tests are described in the next subsections.

2.7.2 Rainfall simulation tests

Rainfall simulation tests of waste rock can be performed by spraying a known amount of water over a designated area to simulate rainfall (Walder et al, 1997; Price, 2009). The water is collected at the base of the designated surface area and analysed for the constituents of interest including, at least, pH, total dissolved solids (TDS), alkalinity, and sulfate and iron content. Rainfall simulation leach tests on exposed rock in pit walls can be performed in the same way as described above for waste rock (Walder et al, 2006), also to evaluate future waste material leaching from rock exposed to weathering. However, this evaluation will require supporting information about hydrogeology, mineralogy, etc., of the waste material.

The one time rainfall simulation test may not, however, result in drainage chemistry that is representative for a natural rainfall. Additional information may be obtained by performing rainfall tests on the same spot several times with short intervals (hours) and with long intervals (weeks/months): short time-intervals to evaluate to what extent available secondary minerals were washed out in the test and; long time-intervals to evaluate the regeneration of secondary products. The time intervals in the latter case should be defined based on the local climate (common time intervals between rainfalls), and may require insulation from precipitation and runoff water.

2.7.3 Long-term field tests

Another way to perform field tests and reduce the uncertainty is to build larger controlled tests pads, with collection of rainfall (lysimeter) or to install continuous monitoring systems within and below waste rock piles. Continuous monitoring may include pH and electric conductivity probes in addition to flow rate measurements. It is essential to have a weather station recording rainfall and temperature in the vicinity of the monitoring system, in order to evaluate infiltration rate and the flow system.

2.8 Key testing variables

2.8.1 General

The key testing variables/conditions for kinetic testing will depend on the objectives of the testing and the material available. When the objectives are defined, the tests protocols can be designed and samples collected. Besides the measurements/monitoring of the water flow and quality, the potential key aspects that may be controlled and adjusted in the laboratory are:

- weight/volume of the material;
- test duration;
- grain size;
- temperature;
- water saturation; and

- oxygen supply/air flow.

The same key aspects (test conditions) will then be important to evaluate in field tests or when test data is applied to field conditions.

The choice of experimental setup is crucial since small differences in experimental design may result in large differences in drainage quality (Lapakko and Berndt, 2009). The availability of minerals, especially sulfides and carbonates, is one of the most important factors controlling the rate of acid development and contaminant leaching at mine sites. Lapakko et al (2006, and references therein) have shown the importance of particle size and available surface area for the development of drainage pH, and its importance when interpreting kinetic test results and modelling. The supply of oxygen and the supply and delivery of water to remove the weathering products are examples of other crucial aspects of kinetic test protocols (Lapakko, 2003).

When the humidity cell is used for testing fine grained tailings material only a part of the reactive surface area is in contact with the humidity and may become oxidized. In this case, diffusion of oxygen becomes rate limiting for the oxidation process. In addition, the low permeability of the material may reduce the flushing of reaction products. An alternative experimental setup for the Humidity cell has been developed with the objective of avoiding this limitation where fine-grained material is impregnated into a porous fabric allowing for high flow rate (Schmiermund, 2006). This will eliminate the risk of oxygen diffusion becoming the rate limiting process for the sulphide oxidation rate for the material in the laboratory setting.

For more heterogeneous and larger grained material, such as waste rock, the crushing required for the Humidity cell will make results deviate from actual field conditions. The influence of grain size on the overall oxidation rate of waste rock has been studied, e.g., Strömberg and Banwart, 1995. In a column test with minimal grinding, only acid generating and neutralizing material that is available to weathering, for example, along fractures or on the surface of rocks will contribute to acid-generation and metal leaching (Maest et al, 2005).

Key testing conditions are described in the following subsections.

2.8.2 Sample size and sample preparation

The sample size for a humidity cell test for waste rocks is commonly 2 kg to 5 kg, while for tailings in the range of 200 g to 500 g. If material to be used for the kinetic testing comes from drilling samples, the amount is limited. The material selected for the first kinetic tests during the exploration stage may come from either drill cores or rock chips of certain interval samples where the interval depends on the mineral/metal target material.

It may be useful to run larger kinetic tests in drums that can take 100 kg to 200 kg. This will result in more representative test results without necessarily giving a high cost increase. This is done in the last stage of exploration where bulk material is being extracted, or as a part of the operation where it is necessary to verify results from smaller humidity cell test run during the exploration stage.

If samples are stored before testing they should be either frozen or dried at maximum 30 °C. This results in the halting of oxidation while avoiding destroying secondary hydrated minerals.

Up-scaling is a major issue when designing the kinetic tests and interpreting the test results, where a small sample is representing a large mass of potential waste material. The kinetic tests performed as part of the permit application are usually run on very small samples relative to the population/subpopulation to characterize. The number of samples analysed using kinetic tests is also small.

Waste rock samples are usually crushed to a diameter of < 6 mm for the humidity cell tests while in reality these small grain sizes represent only a small fraction of the waste material. Smaller grain sizes give a higher surface area per weight and thus an increased reaction rate. Porous rocks have higher available surface area than tight rocks. These issues need to be evaluated, both when setting up the tests and when interpreting the result.

2.8.3 Temperature

Temperature affects reaction rates. The constant laboratory temperature around 20 ºC, is likely to be different from the on-site conditions. Pyrite oxidation is an exothermic reaction and this will often result in an elevated temperature in coarser tailings and waste rocks while the laboratory tests are usually small and open for rapid heat exchange. This is a parameter to evaluate and possibly adjust relative to the material tested, the conditions of the disposal site and the objectives of the tests. See 3.5.6 for discussion on the natural system.

2.8.4 Duration

The necessary duration of kinetic tests depends largely upon the mineralogical composition of the waste material. The kinetic tests should be run until there is a relatively constant rate of release of the key parameters, (see Figure 5; e.g. H+, sulfate, alkalinity).

In some cases, there may be an initial “quasi-steady state” at a neutral pH. This is due to the neutralizing minerals being slowly dissolved due to low oxidation rate at circum neutral conditions. However, when the neutralisation capacity is consumed the acidity will increase. It may take a considerable time to reach this second phase. This time until there is a stable release is called lag time and is the time from the start of the testing (or waste is generated) until a stable release of constituents at laboratory scale or field scale is reached. For waste that has been under oxidizing conditions, lag time refers to testing in columns or humidity cell test where there are different leaching conditions from the field to the laboratory.

2.8.5 Sample selection

Sample selection is performed based on previous analysis that has defined the population, i.e. the predicted total volume of waste material, and the variability within the population. Based on the geological mapping it may be possible to define subpopulations.

The number of samples undergoing kinetic testing is much smaller than the number sent out for many of the other chemical/mineralogical tests due to the long duration and high cost of the kinetic tests. Samples for kinetic tests are selected based on information on:

- grain size distribution;
- mineralogy/mineral distribution;
- static testing (acid base accounting); and
- chemical composition.

If there is a large variability, it may be useful for the interpretation to collect samples representing expected worst to best case with regard to the parameters listed above, e.g. selecting samples with high sulfide and/or carbonate content, samples with medium content and samples with low content. The volume and distribution of each of these three (or more) subpopulations can then be used to make overall assessments of acid generation potential in the waste facility.

2.9 Method summary

Standard kinetic tests methods (humidity cell tests) (ASTM D5744 - 07:2007; Sobek 1978) are used all around the world where there is a potential for acid/neutral rock drainage. The tests are designed to optimize the sulfide oxidation rate with regard to e.g. oxygen supply and saturation of secondary minerals. These conditions are not representative for field conditions and there is often a desire to set up more site-specific kinetic tests, as it is believed that such test could be used to simulate the full-scale disposal scenario at the site.

The design of the detailed test set-up, when using the non-standardized methods, may be difficult and may require more columns with variation of the local setting parameters that deviate from the standard method. These tests will, however, often give valuable additional information to the standardized tests.

Lysimeter and field tests will typically be set up during operation and are in most cases not applicable in the early stages, permitting, of extractive projects due to the limited amount of test material available and due to the duration of the tests. Table 1 gives a summary of the main kinetic tests used within the extractive industry. The output data is commonly flow/volume and chemical composition of the drainage water possibly in combination with analyses of the solid waste material before and after the tests. The analyses of the solids are performed in order to evaluate the degree of leaching and potentially remaining secondary products.

Table 1 — Summary of kinetic test methods most applicable to waste from extractive industries. Note that performing tests on/in a facility in operation may present specific safety issues and that installations may be destroyed by vehicles and ongoing waste disposal. Test results may be influenced by ongoing deposition

Method	Setup	Pros	Cons
Humidity cell	Standardized, weekly rinse, humid-dry air flow, optimized oxidation rate; column for waste rocks; “bath tub” for tailings; laboratory scale; coarse tailings up to small grain size (1 cm to 2 cm diameter) waste rocks	Bulk sufide reaction rate, leachate water quality; easy to handle; both acid reaction and neutralizing reaction	Difficult to scale up; long term;
Column test	May be site specific, possible to test reaction rate based on the setting and closure options; laboratory to field scale; tailings and crushed waste rocks	More applicable to the site conditions, leachate water; both acid reaction and neutralizing reaction	Difficult to scale up; long term; border conditions need to be under control, cost
Lysimeter	Collection pad under or within waste material; field scale; natural grain size may be possible	Applicable to seepage water quality; both acid reaction and neutralizing reaction,	Hard to predict long-term seepage water quality without additional data; require large volume; often broken, large size
Field test a) surface test	Collecting simulated/natural rainfall on specific areas and collection of run-off; old waste not new	Run off water quality; rapid test; assuming the dump exists and that the material has been exposed to atmospheric conditions long enough to be representative of stable conditions	Problematic to interpret long-term seepage water quality; poor control
b) pile test	Instrumentation within pile together with lysimeter; natural seepage collection from operating/closed waste piles/ponds; natural grain size	Applicable to seepage water quality; testing closure option in large scale; both acid reaction and neutralizing reaction	Long term (often several years), research oriented; require large volume;

3 Interpretation and evaluation

3.1 General

It is necessary to clearly define the testing objectives to select and design kinetic tests appropriately to obtain the desired information for interpretation and evaluation of the data. Objectives may be to:

- assess if the material is going acidic or not;
- define sulfide oxidation rate;
- define neutralization reaction rate;
- assess when the material will go acidic;
- estimate leaching rates and drainage chemistry; and
- evaluate closure options.

To define if the material will go acidic or not it may be sufficient to monitor the pH of the leachate. However, obtaining data to calculate the bulk oxidation and neutralisation rate of the material being tested will give a better understanding of whether the pH conditions obtained will be sustained in the long run.

The laboratory scale tests may give a good control of individual processes and different tests can give information about different processes; humidity cell tests give oxidation rates at full oxygen supply conditions; column tests can be run with reduced (controlled) oxygen supply; and batch-reactors can quantify neutralizing reactions. However, the applicability to field conditions requires an understanding of how the processes in the laboratory humidity cell tests relate to the processes in the full-scale waste dumps.

It is common to calculate the sulfide oxidation rate based on the sulfate release rate; however, the oxidation rate may also be calculated based on the oxygen consumption rate. Understanding the processes within the test, whether they are small humidity cell tests or large field tests, is essential for the interpretation of both sulfide oxidation and leaching rates.

It is possible to estimate/calculate mineral oxidation rates from humidity cell test data. It is necessary to be cautious when performing up-scaling to field conditions. Up-scaling will often require additional supporting information about the configuration of the waste material and hydrogeological data. This is especially important when it comes to estimating long-term rates. Experimental designs that allow controlled site-specific conditions may be more suitable for this purpose.

3.2 Reaction rates

3.2.1 General

In the scientific literature, mineral reaction rates are commonly given as the amount of mineral (moles) reacted per time unit and surface area (Nicholson and Scharer, 1994; Rimstidt et al, 1994; Williamson and Rimstidt, 1994). The literature is usually referring to pure minerals and not bulks material, i.e. rock with mixed mineralogy. Information on the surface area of specific minerals within the material is required in order to compare test results with published data on pure minerals, information that is difficult to establish for a specific mineral within a rock material. Reaction rates are given per mass unit of waste of known sulfide content and related to the sulfide content. The substantial difference between reaction rates that implies the need in kinetic testing in every specific case is both a resultant of a sulfide exposure within a rock material, and the mineralogic, textural and structural differences between sulfides itself that influence their reactivity.

The overall oxidation process of iron sulfides, represented by the most common sulfide mineral, pyrite, may be expressed as follows:

$$FeS_2(s) + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3(s) + 4H^+ + 2SO_4^{2-} \qquad (1)$$

The oxidation of other metal-sulfide minerals may be described by similar overall reactions. However, it should be noted that not all of the sulfides will generate stable metal oxy/hydroxides or generate acidity under natural conditions (e.g. galena, sphalerite).

The reaction rate may be dependent on the secondary minerals formed and whether or not these secondary minerals are effectively washed out during the rinse cycles. If not, the reacting minerals may become encapsulated which would lead to a reduction of the oxidation rate of sulfides and availability of the neutralising minerals.

Formula 1 shows that, apart from the properties of the sulfidic mineral itself, the availability of oxygen is the major limiting factor determining the actual reaction rate under real exposure conditions. Humidity may in theory affect the reaction rate, however, under field conditions humidity is normally not a limiting factor inside a waste facility. However, water saturation may drastically reduce the oxygen availability and thereby the oxidation rate.

Mineral reaction rates for neutralising reactions are discussed in the overall guidance document (CEN/TR 16376). Neutralising reactions are indirectly being assessed in the kinetic tests by analyses of the leachate. The leachate collected represents the result of the reactions taking place within the material being tested: i.e. sulfide oxidation; mineral dissolution including carbonate minerals; silicate mineral weathering; and mineral precipitation. Carbonate minerals can dissolve at a higher rate than sulfide minerals oxidize and may be buffering the drainage to a neutral pH, while silicate minerals are reacting at a lower rate and need a longer contact time to react and effectively consume hydrogen ions.

As long as carbonate minerals are readily available they will dissolve and consume the acid produced by sulphide oxidation. Alumino-silicate dissolution, which is normally kinetically controlled, may contribute to the acid consumption in a varying degree depending on the acid production rate and it may become significant in materials with a low sulphide content at low temperature or at low oxygen concentrations.

The test results can, as a first step, be interpreted based on the pH measurements of the leachate after the system has come to a steady state release/oxidation rate, as follows (modified from BC ARD Guide, 1989):

- pH < 3 acid generation with little or no neutralization;
- pH 3 to 6 indication of acid generation with partial neutralization;
- pH > 6 no indication of significant acid generation.

In addition, the results from the tests may give a possibility of calculating the bulk oxidation rate for the material. The results may also make it possible to evaluate/calculate the leaching rates for elements within the designed test system.

The reaction rate of sulfide oxidation within the mixed waste material can be calculated in at least two ways from the kinetic cell test results:

- through sulfate release rate; and
- through oxygen consumption rate.

These two approaches are discussed below.

3.2.2 Sulfide oxidation rate, assessed by sulfate release

Duration and rate of sulfide mineral decomposition due to oxidation under stable exposure conditions is a regular process. It can be expressed in terms of half-life of sulfide sulfur ($t_{½}$ days) that reflects both total sulfide sulfur content in a waste material and a reaction rate. Sulfide oxidation rate and sulfate generation can be described by a first order kinetic formula (Caruccio, 1975) and presented as a regular straight line:

$$\mathrm{S}_t = \mathrm{S}_o \exp(-kt) \tag{2}$$

where

S_t is the residual sulfide sulfur content in waste rock after a period of time *t* since the beginning of the test, in wt. %;

S_o is the sulfide sulfur content at *t* =0 (at the start of constant sulfate release), in wt.%;

k is the ln $2 \cdot t_{1/2}^{-1}$ kinetic constant, in days^{-1};

t is the time since *t* = 0 , in days.

For the purpose of evaluating the kinetic tests Formula (2) can be re-arranged to:

$$k = \frac{lnS_0 - lnS_t}{t} \tag{3}$$

The sulfide sulfur content S_0 at *t*=0 is calculated as the initial total sulfur subtracted by the measured sulfate sulfur release during the lag-time, assuming that all non-sulfide sulfur minerals and/or compounds have been leached out during the lag-time.

The residual sulfide sulfur content after time *t* is calculated as S_0 subtracted by the measured sulfate sulfur release during the time *t*.

For new waste (not previously exposed to air) the lag time may be significant, while optimal conditions for sulfide oxidation are developing. E.g. pH is dropping, ferric iron is building up, smaller amounts of rapid neutralizing minerals are consumed, temperature is increasing, and microbial activity is increasing.

Reaction rates assessed from the humidity cell tests are often considerably higher than actual field values for two major reasons:

- sulfide oxidation is a surface process. In the test, a ground material is used, thus the exposure of sulfides is higher than in a natural material of a coarser grain size, and
- access of humid air to sulfides is optimal under typical test conditions (depending on the set-up).

For reaction rate assessments in all discussed kinetic test methods (humidity cell test, column tests, lysimeter and field tests), the measured parameter is sulfur (as sulfate) release over time related to total initial amount of sulfide sulfur (in mass or equivalent units).

Reaction rates determined in the humidity cell tests reflect the specific iron disulfide (pyrite) reactivity, when no other limiting factors occur. This feature is an intrinsic material property of the sulfides themselves and indicates the development of their specific surface, which depends on the crystallographic characteristics of the sulfide mineral.

In many cases, column tests will also require crushing, leading to an increased surface area. However, exposure conditions may be closer to field conditions compared to the humidity cell, all depending upon the test design used.

The exposure conditions and thus the reaction rates are closest to actual field values in lysimeter and field tests. With these setups, precipitation, temperature and other factors may also better represent real field conditions, which again may result in a need to run the test for much longer time periods.

3.2.3 Sulfide oxidation rate, assessed by oxygen consumption

During sulfide oxidation where oxygen is the oxidizing agent oxygen, O_2 (g), will be consumed. The overall pyrite reaction is given in Formula (1), where iron is oxidized from ferrous to ferric and sulfide to sulfate. If pyrite is the main oxidizing mineral measuring the oxygen consumption can be used to assess the oxidation rate. The pyrite oxidation rate (R_{FeS2}) can then be calculated by the following formula:

$$\mathrm{R}_{\mathrm{FeS2}} = \frac{(\mathrm{P}_{\mathrm{I(O2)}} - \mathrm{P}_{\mathrm{(F\,O2)}})}{t \times 3{,}75 \times M_{\mathrm{Py}}} \tag{4}$$

where

R_{FeS2} is the rate, moles/(kg x day);

$\mathrm{P}_{\mathrm{I\,(O2)}}$ is moles O_2 initially in the confined space;

$\mathrm{P}_{\mathrm{(F\,O2)}}$ is moles O_2 at the end of the measuring period, in the confined space;

t is the time, in days;

M_{Py} is the mass of pyrite in the sample at start of oxygen depletion measurement, in kg;

3,75 is the ratio of moles of O_2 per mole of pyrite.

Measurements of the oxygen depletion can be performed during the regular humidity cell/column tests. The volume of the column used needs to be known. The column should be sealed and oxygen (and CO_2) should be measured frequently over a time span of a few days. The duration depends upon oxidation rate and sulfide concentration. The bulk oxidation rate can then be calculated (a similar field method was described by Ritchie, 1994).

3.3 Leaching rates

Obtaining information on the leaching rate of different constituents may be very useful in order to calculate mass loadings from the waste material. In this context, leaching rate refers to the amount of element leached per mass and time unit. The leaching rate in the field will depend on a number of factors and, for waste subject to weathering, will change over time. In addition, the actual release in the field will be limited by processes along the transport route through the waste and surrounding soil, e.g. precipitation of secondary minerals and adsorption to particles.

The standardized Humidity cell is designed to optimize oxidation, which will have a significant impact on overall leaching rates. Lapakko (2003) indicates that the leaching rates for the standardized tests are 1 to 2 orders of magnitude higher than in the nature. There are standardized leaching tests available that may be applied to extractive waste (see CEN/TR 16376). Nevertheless, if applied properly, using site specific conditions, data from kinetic tests can provide knowledgeable experts information on leaching and in particular, with other data, contribute in evaluating how leaching may develop over time. Calculation of the punctual leaching rates (LR) can be performed using Formula (5) (Morin and Hutt, 1997; Price, 2009.)

$$\mathrm{LR} = \frac{c_{\mathrm{r}} \text{ x } V_{\mathrm{r}}}{M_{\mathrm{S}} \text{ x } t_{\mathrm{r}}} \tag{5}$$

where

LR is the leaching rate given as mg constituent leached per time (s) per kg of waste material;

c_{r} is the constituent concentration in the rinse, mg/l;

$V\mathrm{r}$ is the volume of the rinse, l;

$M\mathrm{s}$ is the mass of the sample, kg;

t_{r} is time between each rinse interval, s.

The optimum concentration to use for this calculation is when the release rate has stabilized (constant concentration). If based on sulfate concentration in the rinse this leaching calculation will represent the sulfide oxidation rate as a function of time, in some cases together with dissolution of other sulfur containing minerals as discussed above.

When using kinetic test data to evaluate leaching it is important to understand the processes controlling acidification and the main factors affecting the oxidation and leaching rates. The main controlling factors are:

- grain size distribution;
- amount of rainfall;
- the chemical environment controlling release (e.g. pH, redox conditions, DOC); and
- temperature.

Specific aspects to consider when assessing field conditions based on humidity cell or column test data will include:

- the water may percolate more rapidly through the cell than in the in the full scale waste dump or pond;
- there are limiting factors in the nature that are (intentionally) circumvented in the test cell (oxygen availability, elements that are inhibiting the microbiology, silicate reactions);
- secondary mineral build-up in the waste deposit may not take place in the cell due to higher liquid/solid ratio in the tests compared to field conditions;
- micro, matrix, macro pore flow interaction; and
- long term changes not captured in the test cells (e.g. change in surface area due to weathering, porosity changes due to mineral changes).

A complete simulation of field conditions is not possible. Thus the objective can never be to exactly predict drainage water quality at all times and under all conditions, but rather to get un understanding of how the facility may perform over time and under various scenarios. The best (only) way to take issues such as those mentioned above into account is through geochemical modelling, preferably reactive transport modelling. For this purpose various modelling tools have been developed (CEN/TR 16376)

3.4 Leaching result evaluation

Based on the results from the kinetic tests, it may be possible to evaluate mineral reactions in the system (Figure 5).

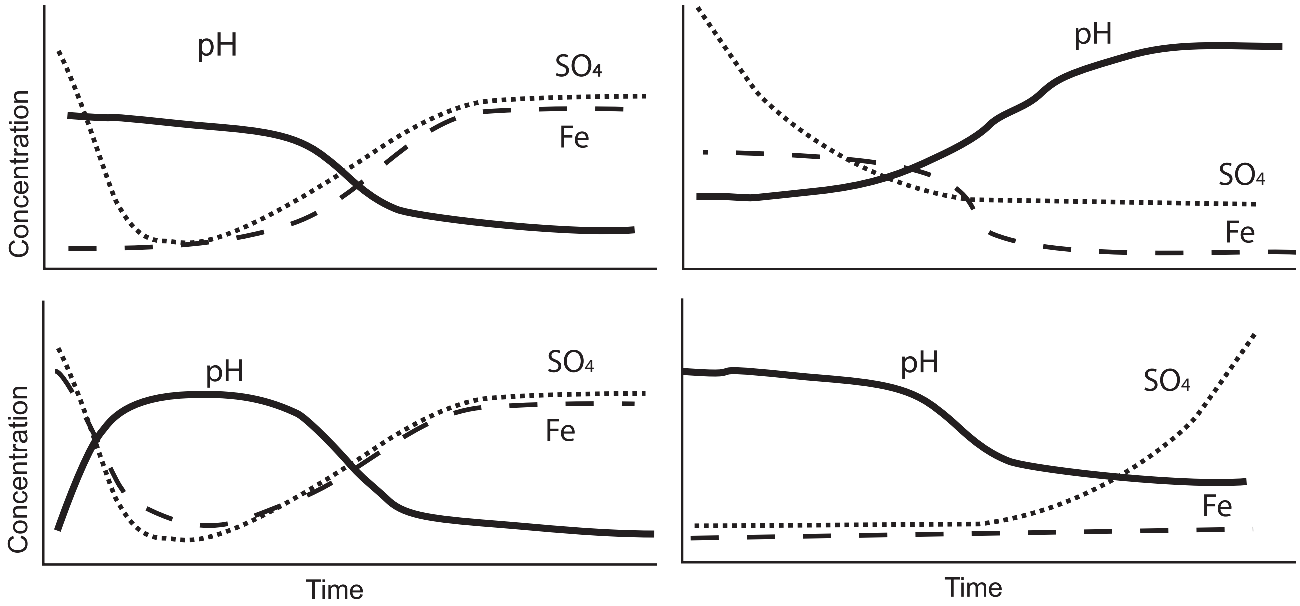

Figure 5 — Illustration of a possible kinetic test result. See text for explanations (from Walder and Schuster, 2003)

- The top left graph in Figure 5 illustrates a sample that contains an easily soluble sulfate mineral (e.g. gypsum) that does not generate acid when dissolving, however, with time the sample is an acid generator.
- The lower left graph illustrates a sample containing easily soluble acid generating sulfate (e.g. jarosite). After an initial wash out of the easily soluble sulphate the sample is well buffered, but with time it is going acidic.
- The right top graph illustrates material that has secondary minerals generating acid, but with time shows net neutralizing capacity (increasing pH) and due to this, iron and sulfate drops. Iron may precipitate as iron hydroxide shown by a sharp decrease halfway into the tests, while sulfate may be limited by gypsum precipitation.
- The bottom right graph illustrates a sample that with time is going weakly acidic and iron is not released due to precipitation of secondary iron hydroxide minerals, while the release of sulfate increases with time, likely due to oxidation of non-acid generating sulfide minerals. There may also be weak acid generation together with acid-neutralisation and thereby a moderate decrease of pH together with high sulfate.

The results from the leachate analysis should be evaluated together with mineralogy/mineral chemistry, element distribution analysis (sequential extraction, pH dependence test) and possibly modelling, to be able to understand the processes within the tested material. These mineralogical and chemical analyses can be performed prior to and after the kinetic testing when the solid material can be sampled. Results are compared before and after test.

3.5 Application to field conditions

3.5.1 General

There are many different factors/parameters that control the reaction rate of minerals and the outcome of kinetic tests. This section discusses key controlling factors and how test results may be evaluated to provide useful information for an operation, e.g. how test results may be applied to full-scale field conditions.

Laboratory temperatures and redox conditions deviate from field conditions, and these deviations may result in under- or overestimation of metal leaching and acid production rates. The humidity cell tests are conducted under unsaturated and highly oxidising conditions and are not intended to simulate acid production or contaminant leaching under more anoxic or under fully saturated conditions (Price, 1997, 2009). Under such conditions, where sulfide oxidation is in practice halted, column tests may better simulate the leaching processes that are likely to take place in the waste facility.

The field of kinetic testing for predicting potential environmental effects and evaluating mitigation/reclamation options is under development. The column tests can be very useful in evaluating different remediation options such as waste mixing, lime treatment, and cover systems. From these tests and evaluations, treatment systems may be designed or improved. A review of recent literature on these issues is incorporated in this section, to provide information about possible additional tests or improvements to those tests that have been run. Specifically, the test methods are reviewed with respect to the following test parameters:

- mineralogy/mineral chemistry;
- particle size;
- texture;
- air flow rate / oxygen exposure;
- temperature;
- microbes;
- leaching rate; and
- duration of test.

All these parameters are important for the weathering rate, oxidation, dissolution, and precipitation of the rocks/minerals that are being tested.

3.5.2 Mineralogy/mineral chemistry

Iron sulfide minerals (e.g. pyrite, pyrrhotite, marcasite) are the most acid generating minerals, i.e. they can generate the most acid per mass mineral (overall guidance document, CEN/TR 16376) and more in detail in the GARD Guide (2009), Price (2009)). Pyrite is the most common sulfide mineral, however, other sulfide minerals (e.g. pyrrhotite) may have higher oxidation rates.

The mineralogy and mineral chemistry are the prime controlling factors for the quality of the drainage from waste material generated by the extractive industry. A thorough understanding of the mineralogy of the material, before and after the test, is therefore important in order to correctly interpret the test results.

Different minerals have different dissolution/precipitation reactivity controls, e.g. microbiology, redox potential, pH, and ion concentration. Different minerals have different impacts on water quality. Some are a source of metals, some contribute alkali elements, some generate acidity and some remove acid. The overall guidance document (CEN/TR 16376) briefly discusses these issues.

During the test period there may be changes to the mineralogy, e.g. mineral alteration and secondary mineral precipitation. These mineralogical changes may also result in a change of water quality.

Analyzing for secondary minerals using e.g. sequential extraction, pH dependence tests, scanning electron microprobe (as described in the Overall Guidance document), before and after the material has been subjected to the kinetic testing, may aid in understanding the processes taking place within the column.

3.5.3 Particle size

Larger particles have smaller surface area per mass than smaller particles and larger surface area increases the oxidation rate as shown for pyrite by Nicholson (1994). This does not necessarily mean that tailings oxidize faster than waste rocks since oxidation of tailings is often limited by oxygen availability.

There are methods available to analyse specific surface area and this information, together with the mineral composition, will be needed in order to apply test results to the evaluation of waste dumps and tailings facilities and to adjust the reaction rate to actual grain sizes (see CEN/TR 16376). If the grain size distribution of the material within the columns is the same as in the dumps there is no adjustment needed for grain size.

3.5.4 Texture / hydraulic conditions

Texture defines the general character of a rock, shown by its component particles in terms of grain size and shape, degree of crystallinity and arrangement. The texture exerts an impact not only on "hydraulic conditions" (including air penetration), but also susceptibility to weathering and decomposition and on conditions of generation/release of constituents.

The texture and hydraulic properties of the material are significant factors governing the contact with water and air in the kinetic test cell (laboratory column or field set up). At site scale, the (physical) heterogeneity in the waste dump will give rise to non-uniform flow fields (preferential flow-paths), which will have an impact on the contact between water, air and waste and the transport of weathering products.

Texture and hydraulic conductivity will be very different in the laboratory tests relative to the field conditions. With a good understanding of these differences it is possible to make the necessary adjustments to relate laboratory test data to field conditions. The issues of textures and hydraulic conductivity are discussed further in the overall guidance document (CEN/TR 16376).

3.5.5 Air flow / oxygen exposure

To optimize the oxidation rate in humidity cell tests, air is pumped through the column. In a waste dump with sulfide oxidation air convection may take place due to oxygen consumption and temperature increase. Tailings on the other hand, have low hydraulic conductivity and the development of a convective system is unlikely.

González-Sandoval et al (2009) reported that there were significant weathering rate differences between high and low airflow in kinetic testing. The difference was attributed to drying of the sample; sample drying took place more rapidly in the high airflow sample, thus reducing the oxidation and, therefore, resulting in a lower oxidation rate. If tests are run with humid air only, this should not be an issue.

3.5.6 Temperature

Weathering rates are higher in higher temperatures due to lower activation energy at higher temperature. Almost all laboratory kinetic tests are performed at room temperature, while larger field tests are performed at field temperature. In strongly oxidizing waste rocks in a waste rock dump the temperature can get up to 50 °C to 60 °C, or even higher, due to the exothermic reaction of pyrite oxidation. Elevated temperatures above normal laboratory temperatures may also favour the thermophilic organisms that are capable of oxidizing iron and sulfur (Ehrlich, 1978; LeRoux, et al., 1979), while population of thiobacillius ferrioxidance will decline at elevated temperatures (Murr and Brierley, 1978). The columns used in the laboratory are often relatively small and it is unlikely that elevated temperatures will develop within the columns. This means that the rate estimated in the laboratory may be too low relative to what may take place in the field, assuming that temperature is the most significant parameter that differs between the field and the laboratory tests.
If this is an expected effect, it may be advantageous to run the laboratory tests at an elevated temperature.

3.5.7 Microbes (inhibitors/enhancers)

The practical significance of microbial activity for the oxidation of sulfides is still subject to debate. It has been shown that microbes can enhance the sulfide oxidation rate and it has been argued that in many settings they can be a very important part of the oxidation process (Schippers, et al, 2010; Hallberg, et al, 2010). For some sulfides, e.g. sphalerite, there are indications that microbes are not affecting the sulfide oxidation (Stanton, 2008).

The microbes are, or may become, available if the samples are not kept sterile. However, for microbes to become active, the conditions need to be favourable for their sustained survival and growth. This implies the presence of nutrients, as well as the absence of inhibiting levels of toxic elements (Cd, Hg, As, Sb). Inhibition by toxic elements may be temporary until these elements have been washed out, bound in a form that no longer inhibits microbial growth, or the microbes become adapted to the environment.

The effect of microbial activity may not show until weeks or months after starting the tests. This may be due to lack of nutrients, the presence of readily available neutralizing minerals (the most active sulfur and iron oxidizing bacteria require acidic conditions) or due to inhibition of bacterial activity.

3.5.8 Test duration

The early humidity cell test protocols and kinetic tests were designed to last for 20 weeks (Sobek et al, 1978). If material have been weathering for several years (old tailings and waste rocks), 20 weeks may be sufficient. However, for fresh samples, even one year may not be sufficient; especially for material with a low content of both sulfides and acid consuming minerals. For this type of material acid generation and the consumption of neutralising minerals may be slow and it takes long time for the material to go acidic. When the acid consuming material is depleted and the pH decreases the conditions for the main sulfide oxidizing microbes improve which may further increase the oxidation rate.

The duration of the tests should be decided based on the objective of the test, monitoring results of the tests performed and on the knowledge of the mineralogy. If the composition is such that the neutralizing minerals may be predicted to be depleted, these should be consumed before the tests are halted.

Field experiments may have to be run for several years, before useful information for evaluating acid generation, leachate quality, and closure options etc. may be obtained.

3.6 Field test evaluations

3.6.1 General

In-field reaction tests may be the most applicable test method to use for prediction of acid generation and metal leaching. However, these tests are often not an option during the permitting phase before the start of a new operation. The field tests may be e.g.: tests to simulate field conditions on material that has been exposed to weathering for some time; scaled up laboratory tests; and tests to evaluate closure options.

3.6.2 Rainfall simulation tests

To evaluate runoff water quality, rainfall simulation tests can be performed. Samples collected from rainfall simulation tests may be fairly representative of runoff water quality from the next rainfall from the area sampled. However, this assumes that:

- the amount of water (mm/m^2) used in the tests is representative for a normal rainfall;
- there is no continuous build-up of soluble secondary minerals; and
- the location for the leach test is representative for the waste material or exposed surface area sampled.

To evaluate the effect of variations in precipitation (intensity and amount), tests can be performed with varying water supply. This will likely result in different constituent concentrations in the collected runoff, but may give the same mass loading. The result can be evaluated together with knowledge about the type of rainfall that is typical at the site (downpour, many smaller rainfalls, long term drizzling, etc.).

To circumvent the issue of accumulation of soluble secondary minerals, tests can be performed on the same location several times with different time intervals. This will give indications of the reaction/release rate and can be useful in evaluating both runoff water quality and mass-loading.

3.6.3 Long-term field tests

Another way to perform these tests and reduce the uncertainty is to build larger controlled tests pads (lysimeters), with collection of drainage or to install continuous monitoring systems below the waste rock pile.

Continuous monitoring will have to focus on parameters where the probes are not too sensitive to outdoor conditions, for example pH and electric conductivity in addition to flow rate. It may be essential to have a weather station recording rainfall and temperature in the vicinity of the monitoring system for better evaluation of the seepage flow volumes and thereby the geochemical data.

Continuous monitoring of runoff water from rock surfaces may be difficult due to sporadic runoff. Sampling of the runoff could rather be performed after each (or several) rainfall event(s).

The drainage from tailings and mine wastes may recharge groundwater and/or discharge to surface water. Monitoring of discharge water quality is usually required during production and post-closure. This information may be used to support the evaluation of leaching rates.

Information from field tests may be used to:

- calculate residence time for water within the waste material;
- distinguish matrix and macro flow;
- calculate, on a mass balance level, processes taking place within the waste material;
- evaluate long term and short term neutralization potential;
- calculate/estimate the long-term leaching potential and drainage quality;
- calculate mass loadings; and
- evaluate/calculate the effectiveness of different mitigation options.

If seepage from tailings dams or waste rock dumps is used to calculate leaching rates, continuous monitoring (e.g. flow rate, pH, TDS) and collecting bulk water samples is the best method, especially for waste rock. If samples are collected and measurements performed only during and immediately following rainfall events this data may not be very representative of what leaches out later during the rainfall or over time. It only represents a spot measurement.

EXAMPLE: In dry climates, most of the leaching takes place as a response to rainfall events. The elemental concentration in the leachate will most likely reach its peak in the early phase of the event and drop as the rainfall continues (wash-out). However, the total amount leached and the development over time depends on the amount of material that has been oxidized, the amount of rainfall, the reactions taking place during the leaching and transport, and the hydraulic properties of the material. So the questions to ask would be:

Is the water sample representative (quality and volume) for the discharge during the short-term seepage period?

Can this water quality and volume be used to calculate the mass loading/water quality for this period/rainfall?

The answer to the first question depends on the material tested (mineralogical and hydrogeological conditions) together with the specifics of the rainfall event. The best way of testing this is to take samples after several rainfall events or having a continuous monitoring system for both quality and volume.

Calculating/predicting long term mass loading is difficult due to the many processes that may take place within the waste material and the heterogeneity of the waste material. Continuous monitoring will help in evaluating if there are differences in leaching water quality with different size of rainfall and with seasonal/climate changes. When this has been sorted out the approach for mass loading calculations and water quality prediction can be defined, and calculations be performed.

4 Recommendations

4.1 General

This Technical Report has been focusing on the flexibility of the kinetic tests for sulfidic waste in order to make the result more applicable to the site in question. However, this requires an understanding of the processes that potentially will take place within the waste material after deposition and also an understanding of the design variables for the kinetic test set-up. The objective(s) of the study will to a large extent dictate the design of the tests together with site-specific issues.

The potential objectives of the kinetic tests are described in introduction to Clause 3. Site-specific issues may be:

- available material;
- topography and hydrology;
- climate; and
- closure plans (e.g. possible wet cover, mixing fine and coarse grained material).

In general, fine-grained tailings with low hydraulic conductivity are not suited for the regular column or humidity cell tests. Design framework will be discussed based on the objectives listed in the introduction to Clause 3. It is recommended to carry out testing on at least two different grain sizes to evaluate grain size/surface area effects on the reaction rates.

4.2 Assess if the material is going acidic or not

If the purpose is to evaluate the potential for the material to go acidic, the standard Humidity cell (Price (2009), ASTM 2007) may be appropriate, at least as a first approximation. In general, the test should be run until the release rate of sulfate has stabilized. The time frame for this can be several months to several years. If the mineralogy is well understood the lag-time is possible to predict.

If there is a significant content of easily soluble neutralizing minerals in the material this will result in consumption of produced hydrogen ions and elevated alkalinity in the leachate. This alkalinity needs to be compared with the mineralogy to evaluate if there is excess of the alkalinity-producing mineral relative to the acid producing minerals.

Analysis of pH, alkalinity and sulfate on the weekly rinse solution is usually sufficient. Following the test it may be useful to evaluate if there has been a build-up of secondary minerals, e.g. through element distribution analysis, that can affect the evaluation of the acid drainage potential.

4.3 Define sulfide oxidation rate

The standard method as described in 2.4 is applicable also for defining the bulk oxidation rate for material (intrinsic oxidation rate). The oxidation rate would likely be established under fully oxidizing conditions, and this rate can be used e.g. in modelling where it is possible to include reduced access to oxygen. The discussion in 4.2 on test duration is applicable also for this objective.

4.4 Define acid consuming reaction rate

Defining acid consuming reactions can be done in response to the acid production rate using Humidity cell and column tests and by using batch reactor or flow through reactor in a system where the sulfide oxidation is halted by water saturation. The rapid acid consuming minerals would be calcium carbonate minerals, therefore analysing for calcium and magnesium in the leachate would give indications of acid consuming minerals. Silicate minerals (especially calcium rich plagioclase and mafic minerals) have also a potential to consume acid. It is necessary to have good mineralogy data to be able to estimate the rate and the total potential for acid consumption.

Silicate minerals have the best potential to effectively consume acid where the reaction time in long (e.g. tailings). Reaction rates may be established through the element analysis, but may also be obtained through modelling of the processes using column data (leachate chemistry, mineralogy, test conditions, etc.).

It is also possible to use the up-flow percolation tests, batch tests, and flow through tests to evaluate the acid neutralisation potential rate. These methods are discussed in the overall guidance document (CEN/TR 16376).

4.5 Assess when the material will go acidic

It is recommended to include more site-specific information in assessing when the material will go acidic. This assessment may be important if it is determined from the first kinetic test that the material is likely to go acidic. Assessing when the material is likely to go acidic can be difficult and can take a long time. A mixture of testing and geochemical modelling may be necessary.

The best assessment would be achieved by using the water infiltration rate and climatic conditions from the site. By testing several grain sizes an assessment can be performed of the grain size effect on the mineral reaction rates. The best option may be to perform the tests on site. The tests may be performed in larger drums that can take a few hundred kilograms. The use of drums often has the limitation of being highly affected by the climatic variations, which would only mimic the outer 2 m to 3 m of the waste material but not the inner part. This has to be taken into account in the evaluation.

4.6 Estimate leaching rates and leachate quality

Leaching rates can be calculated from the data obtained from the different kinetic tests – from laboratory scale to field-scale. The applicability of the observed leaching rates depends on how well the tests are simulating the natural setting. The laboratory tests may give first approximations and are often conservative (high leaching rates compared to the natural setting). The laboratory test may indicate that it is necessary to carry out more site-specific testing. The leaching rates may be used in modelling (if enough input data is available) where the external factors (e.g. mineralogy, morphology, geotechnical properties, hydrogeology, and facility design) affecting the drainage chemistry can be adjusted to more site-specific conditions.

It may also be relevant to assess the drainage chemistry even if the material is not likely to go acidic. As described in the overall guidance document (CEN/TR 16376), when sulfides oxidize they may release elements e.g. cadmium and zinc from sphalerite, lead and silver from galena, without the material going acidic.

4.7 Evaluate closure options

Evaluating closure options may require large laboratory scale and fields-scale analysis, using site-specific information, depending upon the waste characteristics and local conditions. Long-term monitoring with the objective of testing different closure scenarios (e.g. different cover designs; layering tailings and waste rocks; mixing waste material) may be set up during operation, when large quantities of waste material are available and the operator has personnel on site. This kind of tests will require instrumentation to evaluate e.g. infiltration rate, continuous monitoring of drainage and seasonal collection of drainage water for water quality analysis. The data collected may be used for hydro-geochemical modelling of the processes that possibly take place in the waste material under investigation.

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