Kinetic tests comparison and interpretation for prediction of the Joutel tailings acid generation potential

M. Benzaazoua · B. Bussière · A.-M. Dagenais · M. Archambault

Abstract Five sulfide mine tailings coming from the Joutel mine tailing ponds (Quebec, Canada) were tested by the humidity cell test (30 to 52 cycles duration) and the column test (11 to 12 cycles duration). The objectives of this study were twofold. First, there was the determination of the tailings acid generation potential for site reclamation. Second, there was the kinetic test comparison for understanding the tailings geochemical behavior under different test conditions. The samples used had a wide diversity in terms of acid-generation potential, particle size distribution, and parameters influencing reaction rates. Leachates produced remained at a near neutral pH for the duration of the tests. Evolution of the main elements involved in the dissolution processes demonstrated neutralization by carbonates as a response to the acid generated by sulfide oxidation. Depletion rates given by sulfates are higher for the humidity cell tests when compared to those obtained for the column tests. This is consistent with most studies to date, the humidity cell test being considered as more severe. However, by taking the ratio between cumulative elements coming from neutralization and the ones coming from oxidation, similar curves (named herein oxidation –neutralization curves) for all tests were obtained. These results show that overall geochemical behavior of the tailings is similar at near neutral pH for both types of tests. With this interpretation method, the acid-generation potential of the Joutel tailings were tested and compared to the static test results to constrain their uncertainty zone with regard to the studied tailings. The tailings geochemical behavior (carbonate dissolution response to sulfide oxidation) at near neutral pH condition appears slightly dependent of test conditions under certain hypothesis.

Keywords Acid mine drainage (AMD) · Sulfide · Neutralization · Prediction tests · Joutel mine site (Quebec, Canada)

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Introduction

Environmental considerations have become an important factor in the economic feasibility of any mining project, especially those with sulfide-rich ores, where acid mine drainage (AMD) can become the main environmental problem. AMD occurs when sulfide minerals within the tailings (mainly pyrite and pyrrhotite but also ore sulfides lost in the milling process) are exposed to the presence of oxygen and water and the possible presence of bacteria like Thiobacillus. In these conditions the sulfide minerals oxidize and produce sulfuric acid that lowers the pH when the neutralization potential of the waste is either absent or exhausted. As the pH drops, the solubility of metals increases and the effluents become contaminated. Many examples of AMD contamination can be found around the world (SRK 1989; Gray 1997; Marcus 1997; Aubertin and others 2002).

The predictive tests used to evaluate the acid-generation potential of mine waste are critical for determining the environmental impact of a mine site and for choosing a waste management method to minimize that impact (SRK 1989; Ritcey 1989; Morin and Hutt 1997; Benzaazoua and others 1998, 2001; Bussière and others 2004). Static tests, kinetic tests, and geochemical models have been developed and are used on a regular basis, primarily to establish if and when a given material will generate acid. Static tests have been so named because they are usually conducted at a given point in time, and do not account for the rate and evolution of the observed reactions. They generally rely on measuring the

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sulfur content to predict the Acidic Potential (AP) of the waste and a titration to estimate the Neutralization Potential (NP). When the results of static tests are inconclusive (these tests have a relatively large uncertainty zone), or when one is interested in the evolution of drainage quality with time, kinetic tests are desirable. More details on static tests can be found in Sobek and others (1978), Lawrence and Wang (1997), and Morin and Hutt (1997).

There are different types of kinetic tests to estimate the reaction rates and depletion time of different minerals; the most common tests are column and humidity cell (SRK 1989; Lawrence and Marchant 1991; Morin and Hutt 1997). The main advantage of the humidity cell test is that it returns data relatively rapidly (test durations range from 20 to 52 weeks) on a smaller volume of material than a column test. On the other hand, the column test is considered to be more representative of actual field conditions (Bradham and Caruccio 1991). Some investigations from previous reports have attempted to compare the different kinetic tests. They demonstrated that, depending on the type of test used and/or conditions during testing, the results in terms of water quality and reaction rates are different (Bradham and Caruccio 1991; Benzaazoua and others 2001; Frostad and others 2002; Villeneuve and others 2003).

To investigate this aspect and to determine the acid-generation potential of the Joutel tailings (tailings for which static tests gave results in the uncertain zone), five representative samples with a wide variety of sulfide content and particle-size distribution were tested using column and humidity cell tests. They were taken at the site and characterized prior to kinetic testing and also after experiment dismantlement to confirm or reject geochemical findings.

The paper first presents a brief description of the Joutel mine site and then the different methods used in this study to evaluate the geochemical behaviour of the Joutel mine tailings. This is followed by the main physical, chemical and mineralogical properties of the studied materials. Finally, the main geochemical and post-testing results are shown and analyzed for the two types of kinetic tests.

Joutel mine site

The samples came from the Joutel tailings pond, which belongs to the Agnico-Eagle company. This site is near the old Joutel city, approximately 195 km north of Val d'Or (Quebec, Canada). The gold mine was in production from 1974 to 1994. Gold was contained in a sulfide-rich portion of a pyritiferrous ore deposit (Barnett and others 1982) The Joutel tailings impoundment covers 120 ha and can be divided into two parts (Fig. 1). The old pond was filled with the Agnico-Eagle tailings (1974–1986), while the new pond contains tailings generated by the Telbel mine operation (1986–1994). Both types of tailings contain sulfide minerals and have a substantial neutralization potential (Blowes and others 1994, 1998).

Different studies have been undertaken to determine the acid generation potential (AGP) of the Joutel tailings impoundment. Golder Associates (unpublished report) did a characterization of the site and used mainly static test results to evaluate the AGP of the Joutel site. Blowes and others (1994, 1998) performed a geochemical, mineralogical and microbiological investigation to determine the potential for acid mine drainage and dissolved metals release from the tailings Joutel site, but were not able to bring a clear statement about the AGP of the site. To further investigate the AGP of the Joutel tailings, a laboratory study using kinetic tests was undertaken and will be presented below.

Material and methods

In this study, column and humidity cell tests were used to determine the rate of acid generation and metal release of five tailings samples coming from the Joutel mine site. The tests were conducted in accordance with known established practices (SRK 1989; Lawrence and Marchant 1991; Morin and Hutt 1997).

Sampling

The five samples were taken at different locations in the Joutel tailings pond. Their selection was based on two sampling campaigns of approximately 100 samples, to take into account the tailings pond heterogeneity (Blowes 1994 and others). The sample locations are presented in Fig. 1. The selection criteria were mainly the sulfur content, the neutralizing potential, and the particle-size distribution. The collected samples were preserved, until the start of the kinetic tests, under water to reduce oxygen contact, which can cause the oxidation phenomena. They were placed into the columns and the humidity cells in a humid state. The five samples have been named BH96–2, BH96–9, BH96–11, BH96–11ox and UQ-8. BH96–11ox represents a prior oxidized material sampled at the pond surface. The corresponding fresh material is BH96–11. The oxidized sample will allow the evaluation of the long-term geochemical behavior as an extrapolation in time.

Analytical methods

Solid tailings composition was determined by Inductively Coupled Plasma (ICP-AES) analysis after acid-bromine digestion. Leachates from testing were also analyzed with the ICP-AES technique for SO_4^-, Ca, Mg, Mn, Fe, Cu, Zn, Si and Na contents. Pore water pH and Eh measurements were made immediately on fresh samples with a pH/mV meter. The redox potential was measured with a platinum electrode and the measurements were corrected to the standard hydrogen electrode by the use of known calibration standards.

A Sobek Acid Basic Accounting (ABA) test (Sobek and others 1978) was performed on solid samples. It consists of an evaluation of the sulfur present in the sample (in the sulfide form) for calculation of the AP and an acid-base titration for the NP evaluation. In this study, the modified

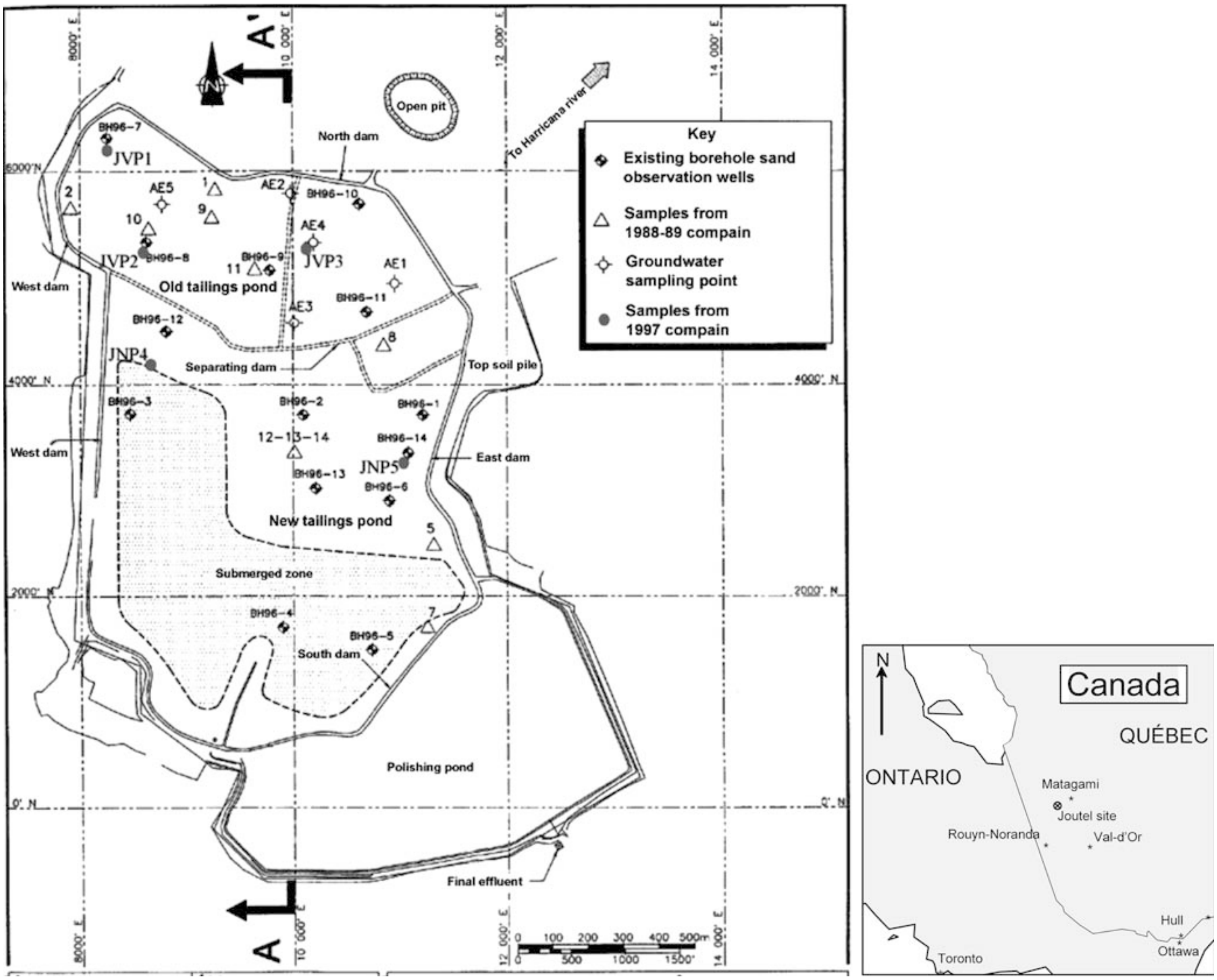


Fig. 1
Schema illustrating the Joutel site, the delimitation between the new and old ponds and the sample localization (Site map modified from Golder 1997, unpublished report)

procedure of the ABA test proposed by Lawrence and Wang (1997) is used. The net neutralization potential (NNP) represents the difference between the NP and AP values. One of the most common classification criteria for the acid-generation potential is the following (SRK 1989):

- if the tailings NNP is higher than +20 kg $CaCO_3$/t, the sample is considered non acid generating,
- if the tailings NNP is lower than −20 kg $CaCO_3$/t, the sample is considered acid generating,
- if the tailings NNP is between −20 and +20 kg $CaCO_3$/t, the sample is in an uncertain zone.

Another useful way to evaluate the AMD production potential using static tests is the NP to AP ratio. Typically, the material is considered non-acid generating if the NP/AP >2.5, uncertain if 2.5>NP/AP >1 and acid generating if NP/AP <1 (Adam and others 1997).

Grain size analyses on the tailings samples were performed with a Malvern Mastersizer, which is a laser-based instrument. The relative density of grains (D_r) was determined with a Helium pycnometer (Micromeritics). Specific surface was evaluated with a Micromeritics Gemini Surface area analyzer.

The mineralogical study was performed by the X-ray diffraction method. The diffractometer used is a Philips equipped with a fix/rotate sample kit and a proportional counter equipped with a monochromator. A scanning electron microscope (SEM) equipped with a microanalysis system (energy dispersive spectroscopy EDS) was also used to study polished sections corresponding to the five samples. The SEM is a pressure vacuum Hitachi S-3500 N equipped with backscattered and secondary electron detectors and a Link Isis microanalysis system from Oxford Instruments. The SEM back-scattered electron (BSE) image mode was used to obtain information on chemical composition variation and relief contrast of the observed zone. The operating conditions were: voltage of 20 kV, current of 150 μA, low pressure in the chamber fixed at 25 Pa and working distance approximately 15 mm. The EDS analyses were performed in the same conditions as imaging. Spectrum acquisition lasted 60 s to 100 s, while x-mapping of the elements took 20 to 30 min for good resolution.

Kinetic testing methods

Column tests

The experiments were performed in vertically mounted Plexiglas® columns placed 2 m above the floor. The columns have an inside diameter of 0.106 m and height of 0.7 m. The bottom of each column is designed to provide water table control using a ceramic plate with a bubbling pressure of 0.5 bar, which also prevents air entry. The water table was fixed 2 m below the bottom of the columns (realistic condition at the Joutel tailings ponds), which were filled with 0.6 m of sulfide tailings. The total duration of the experiment was 1 year with 11 to 12 flush-drainage cycles. Flushes were done with 2 liters of deionized water (pH=6). The drained solutions were recovered at the bottom of the column in an oxygen-free environment and were analyzed for pH, oxidation-reduction potential (ORP), conductivity, SO_4^{2-}, Ca, Mg, Mn, Fe, Cu, Zn, Si and Na contents. A more detailed description of the column can be found in Bussière and others (2004).

Humidity cell tests

Humidity cell tests were performed in a chamber made of Plexiglas® that provided air input and output. The cells have an inside diameter of 0.14 m and 0.35 m height, and were filled with 1 kg of sulfide tailings placed on a geotextile lying on a punched grid. Testing in the humidity cells was performed following the procedure described in Morin and Hutt (1997). The experiments lasted 30 cycles, except for the sample BH96–11 that was tested for 52 cycles. Each cycle was run for seven days. Dry air was passed through the sample container for the first three days and humidified air for the next three days. Dry and humid air flows and temperature were maintained stable for the length of the test. On the seventh day, the sample was rinsed with 500 ml of deionized water (pH =6). The drained solutions were analyzed for pH, ORP, conductivity, SO_4^-, Ca, Mg, Mn, Fe, Cu, Zn, Si and Na contents.

Samples characterization

All samples were characterized for their chemical, physical and mineralogical properties, using the methods presented in the prior section.

Table 1
Chemical analyses of the five studied samples (initial state)

	BH96–2	BH96–9	BH96–11	BH96–11ox	UQ-8
Al (Wt%)	4.82	2.49	4.49	3.24	4.89
Si (Wt%)	16.2	10.5	13.9	11.4	15.4
K (Wt%)	0.43	0.19	0.51	0.4	0.5
Na (Wt%)	2.33	0.83	2.06	1.23	1.92
Ti (Wt%)	n.d.	n.d.	n.d.	n.d.	n.d.
Fe (Wt%)	15.1	23.2	12.8	22.1	15.3
S tot (Wt%)	4.78	10.6	6.36	6.43	5.99
SO_4^- (Wt%)	0.34	0.48	1.91	6.59	0.5
Ca (Wt%)	3.89	4.34	4.31	4.4	4.95
Mg (Wt%)	1.76	1.95	1.58	1.38	2.11
Mn (Wt%)	0.71	0.93	0.48	1.17	0.47
Cu (ppm)	20	25	40	20	80
Zn (ppm)	90	130	110	90	120
Pb (ppm)	40	25	<25	<25	<25
As (ppm)	220	830	520	340	380

n.d., not determined

Chemical characterization

As shown in Table 1, the Joutel tailings have a sulfur content ranging from 5 to 11 wt%. However, a part of the analyzed sulfur is in the sulfates form, especially for the BH96–11ox oxidized sample. The tailings are characterized by significant quantities of calcium (around 4 wt%), magnesium (around 2 wt%) and manganese (around 1 wt%) corresponding to naturally-occurring carbonates in the residue. The remaining mineralogy is represented by silicates and aluminosilicates, as demonstrated by the Si, Al, K, and Na analysis results. In the tailings, the sulfur content is primarily in pyrite. Other sulfide minerals are present in negligible amounts depending on the tailings sample as shown by the zinc and copper grades.

Table 2 summarizes the modified ABA static test results. The acidity potential is corrected by deducing the initial sulfate content of each tailings sample. The NP measurements are similar and reflect the carbonate content of each studied tailings sample. The NNP balance indicates that one of the Joutel samples (BH96–9) is potentially acid generating, and the others are close or in the uncertain zone. These results combined with field observations (no acid generation evidence) justified kinetic testing.

Mineralogy of the Joutel tailings

XRD analysis (Bernier 1998; Geoberex unpublished report) shows that the Joutel samples are mainly made of quartz. The gangue contains, in addition, small amounts of albite,

Table 2
Static test results of the five studied samples

	BH96–2	BH96–9	BH96–11	BH96–11ox	UQ-8
PN kg $CaCO_3$/t	120	150	150	115	180
%S total	4.78	10.6	6.36	6.43	5.99
%S in SO_4 state	0.12	0.16	0.64	2.20	0.17
%S in sulfide state	4.66	10.44	5.72	4.23	5.82
PA kg $CaCO_3$/t	145.8	326.2	178.8	132.1	182.0
PNN net kg $CaCO_3$/t	−25.8	−176.2	−28.8	−17.1	−2.0

orthose, traces of micas, chlorite, epidote and amphibolites. Various amounts of sulfides and carbonates, which are represented mainly by dolomite and calcite in lesser amounts, were identified by XRD in the samples. Some siderite was also detected as well as goethite in the BH96–11ox sample, which is the oxidized correspondent of BH96–11. Gypsum is present in some samples, as seen by the sulfates analysis in the prior section.

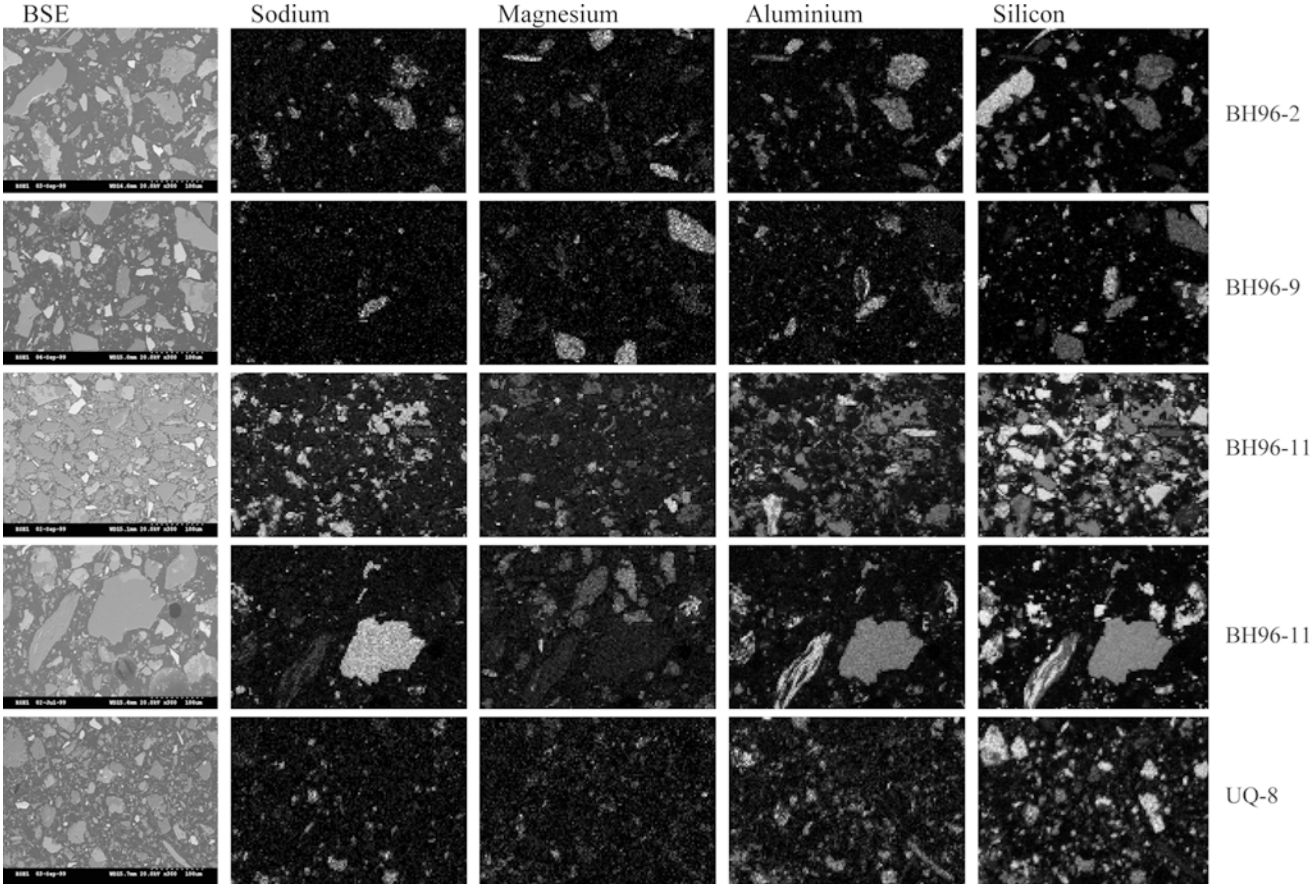
SEM – EDS investigations (Figs. 2 and 3) confirm the XRD findings and allow the distinction between carbonate minerals: dolomite, calcite, manganesiferous dolomite or ankerite and siderite. BSE images for each sample show the grain size and the sulfide content of each sample (brighter grains are sulfidic, gray grains are gangue minerals). The x-map can be interpreted by superposition of the element maps to identify silicates, carbonates and sulfide minerals. Thus, each image can be interpreted as follows:

- Silicon: identification of silicates,
- Aluminum: identification of alumino-silicates from the total silicates (quartz mostly),
- Sodium: identification of silicates containing sodium (ex. albite),
- Potassium: identification of potassium silicates (ex. k-feldspars),
- Magnesium: identification of dolomite by removing all Mg-silicates,
- Calcium: identification of calcite by retrenching dolomite,
- Manganese: identification of Mn-carbonates (ankeritic dolomite),
- Sulfur: identification of sulfide and sulfate minerals,
- Iron: identification of siderite and iron oxy-hydroxides by retrenching all iron sulfides (pyrite mostly and other rare occurrences of pyrrhotite and arsenopyrite described by Blowes and others (1998).

Physical characterization

Table 3 summarizes the main physical parameters of the tailings studied. In terms of grain size analysis, the five tailings studied have non-negligible size distribution differences, but are typical of Canadian mill tailings (Aubertin and others 1996). The mean particle sizes range from 40 to 120 μm (BH96–2 being the coarsest tailings). As demonstrated by the data given in this table, the sample densities are indicative of the mineralogy (presence of sulfide minerals) while the specific surface area reflects the particle-size distribution and the presence of some phyllosilicates well known for their high specific surface.

Fig. 2
Back scattered electron images (scale and magnification are indicated in each image) and EDS X map images showing silica minerals for BH96–2, BH96–9, BH96–11, BH96–11ox and UQ-8 Joutel samples



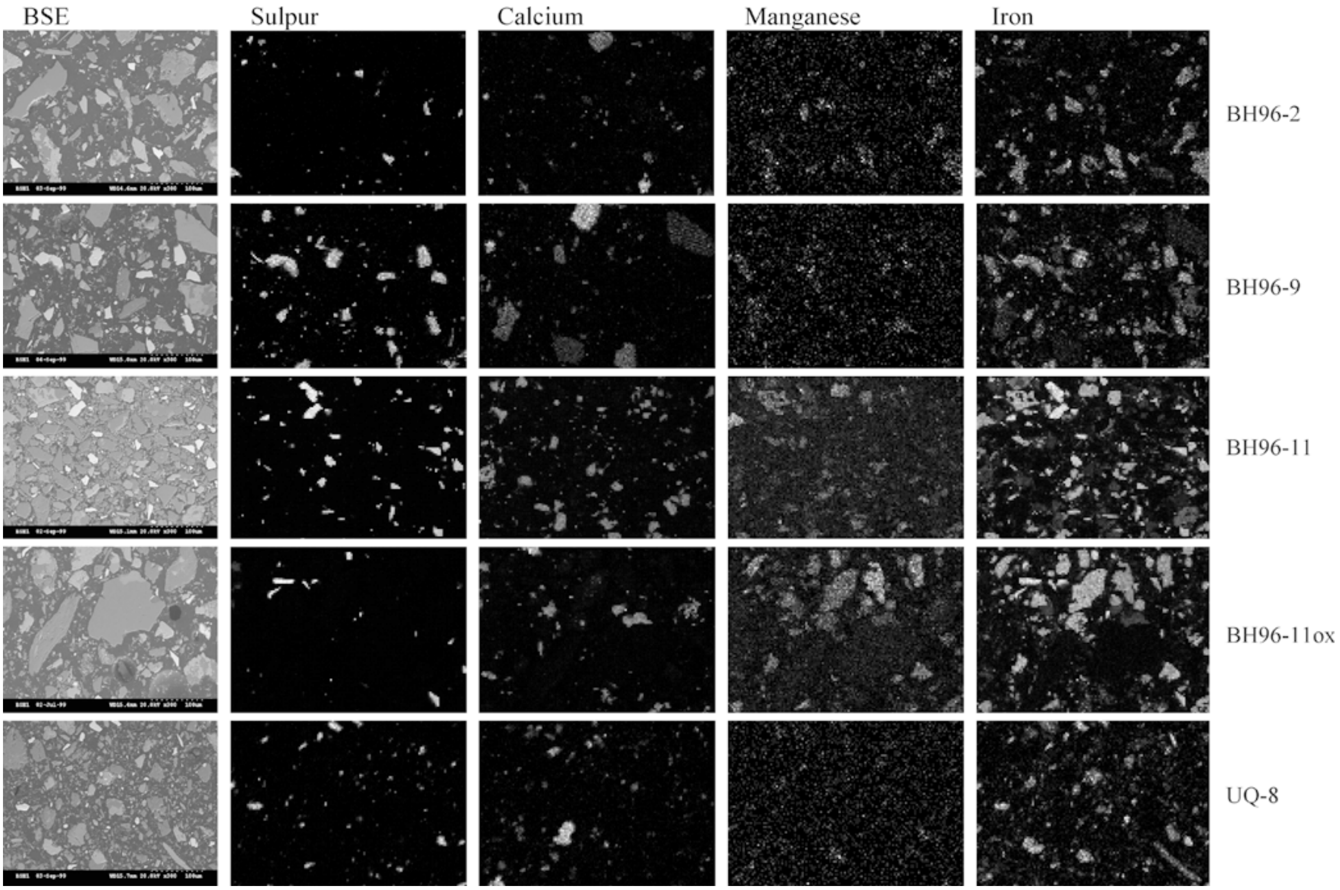


Fig. 3
Back scattered electron images (scale and magnification are indicated in each image) and EDS X map images showing sulfide and carbonate minerals for BH96–2, BH96–9, BH96–11, BH96–11ox and UQ-8 Joutel samples

Kinetic test results

The results of the water quality analysis for both kinetic tests are presented in this section. The evolution of the main elements and parameters involved in the neutralization and oxidation processes are presented (pH, Eh, SO_4^{2-}, Ca, Mg, Mn and Fe). For this study, it can be assumed, as it will be demonstrated, that the neutralization processes are mainly controlled by carbonate dissolution; thus, silicate dissolution is neglected as proven by the very low Na, Al, Si, K concentrations within the flushed water. Figs. 4 and 5 represent the evolution of the measured parameters versus time. The plotted values do not take into account the volume of the recovered waters or the weight of the solid sample.

Table 3
Physical characteristics of the five studied samples

	BH96–2	BH96–9	BH96–11	BH96–11ox	UQ-8
D_r	2.98	3.26	3.00	3.17	3.04
S.S.A. m2/g	0.682	0.845	0.820	1.096	0.958
% under 80 μm	66.6	89.0	89.4	94.4	96.3
D_{10} (μm)	1.9	0.8	1	0.5	0.8
D_{50} (μm)	42.5	16.2	19.2	11.4	9.7
D_{90} (μm)	169.2	80	78.4	54.8	50.6
Mean (μm)	123.2	58.9	61.1	43.1	36.8

pH and ORP variations

The pH remained high (greater than 7) during the experiment for all liquid samples from the two tests (columns and humidity cells), while the ORP increased slightly but remain between 450 and 550 mV/ENH (Figs. 4 and 5). This attests the presence of an oxidant media favorable to sulfide oxidation. The type of test (column or humidity cell) doesn't seem to significantly influence either pH or ORP variations for this material. The conductivity values measured on the flushed waters, not presented in this paper, were often high, attesting to important mineral dissolution. This activity is governed by oxidation and neutralization reactions: carbonate minerals consume the acid produced by sulfide oxidation to maintain the pH at neutral values.

Main oxidation and neutralization products

Many species from the oxidation-neutralization phenomena are detected in the flushed waters recovered from the column (Fig. 4) and humidity cell experiments (Fig. 5). Silicate dissolution is negligible as mentioned above, which demonstrates the small participation of silicates in the whole neutralizing process of the studied samples. This later is assumed mainly by calcium, magnesium and manganese carbonates.

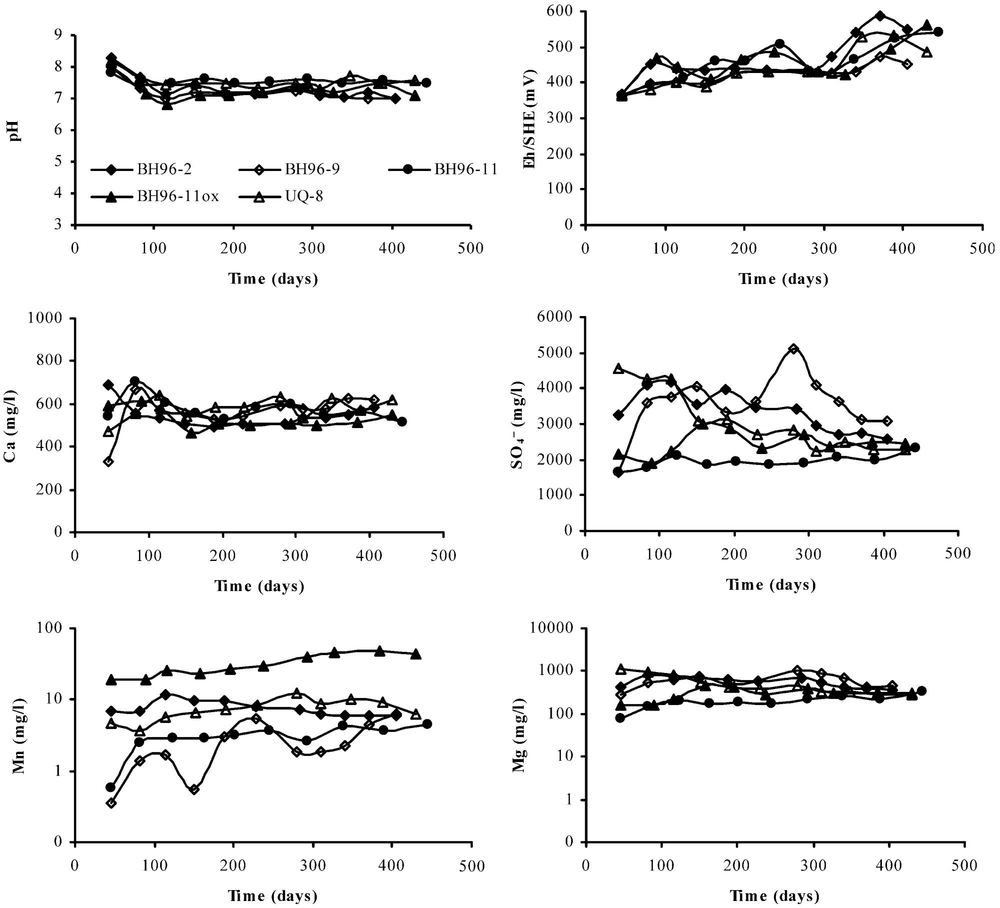


Fig. 4
Water quality corresponding to the Column tests done on the five Joutel samples (instantaneous values)

Calcium, magnesium and manganese

Most of these elements are contained in carbonate minerals, which dissolve when pyrite and other sulfides oxidize. Throughout the test, the pH of the leachates remained high because of the significant neutralization potential of these carbonates in the waste material (represented by the amount of Ca, Mg and Mn in the flushed waters). Moreover, calcium coming from calcite and dolomite dissolution had a constant evolution. Sample BH96–11, submitted to extended humidity cell testing, shows a decrease in this element from the 250th day forth. This attenuation is also noticed for soluble sulfate in the BH96–11 leachate.

Silicon, aluminum, sodium, potassium

These elements come from silicate dissolution. The very low concentrations measured in solution attest to the negligible silicate contribution to the neutralization processes. For example, Si concentrations varied between 10 and 20 mg/l while Ca discharge was around 600 mg/l.

Sulfates

The sulfates are produced by the oxidation of sulfides. Atmospheric oxygen and dissolved oxygen in water reacts with the sulfide minerals between the two flush cycles. The reaction starts at the top of the column, and proceeds downward as the oxygen diffuses through the oxidized layers to the fresh material. Near neutrality conditions mainly involve oxygen as an oxidizing agent (Nicholson and others 1989). In fact, the dissolved ferric iron may contribute little to the sulfide oxidation because of its in situ precipitation as will be seen below. Sample BH96–11, which was tested for a longer time in humidity cell, shows a clear decrease in the sulfate production. It should also be noticed that the evolution of sulfates in the leachates through time follows closely that of calcium for both test types.

Iron

The concentrations of iron in flushed waters from the Joutel tailings were lower than the detection limit of the analysis method even if there is sulfide oxidation as demonstrated by the soluble sulfate presence. As mentioned before, iron precipitates in the samples tested. This will be confirmed with the dismantling of the columns and the humid cell (subject addressed in the next section).

Post experiment characterization

The concentration measured in the flushed solutions do not always reflect the geochemical processes occurring within the solids submitted to kinetic testing. In fact, precipitation often occurs to a greater or lesser extent during testing. For the interpretation of both test types conducted in this project, a post closure solid study was performed on solid chemistry.

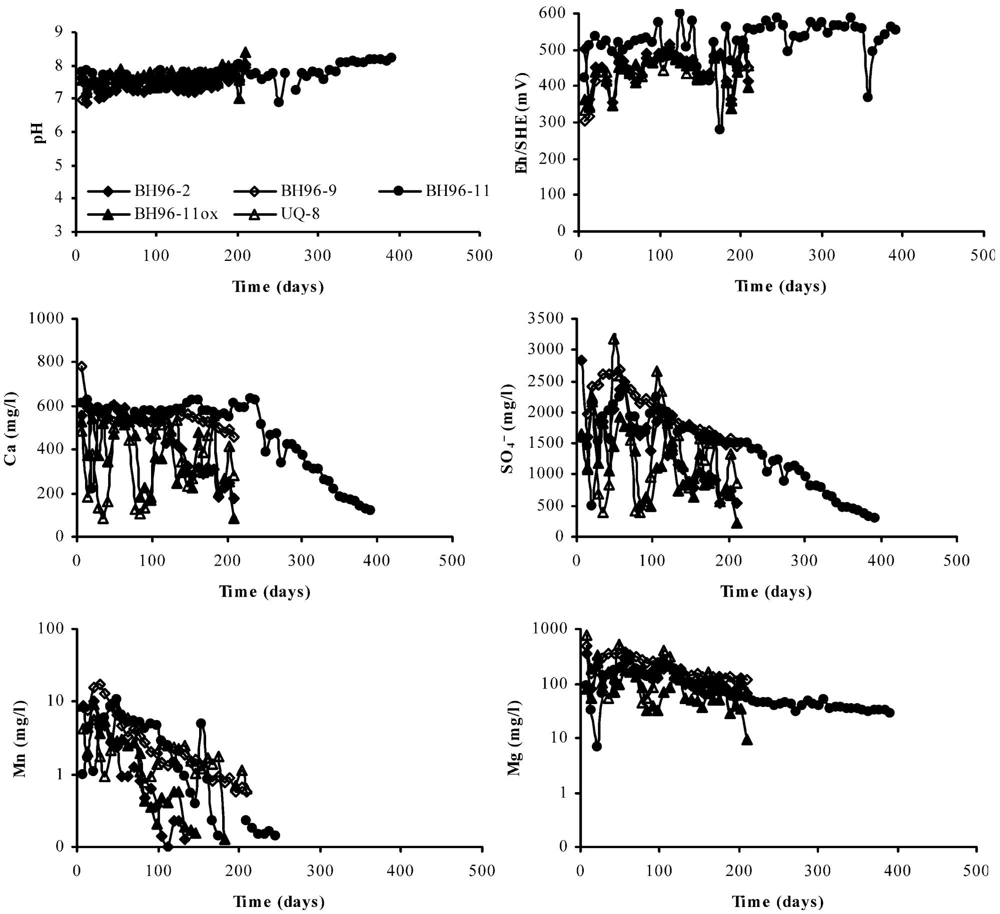


Fig. 5
Water quality corresponding to the humidity cell tests done on the five Joutel samples (instantaneous values)

Post testing results: column tests

During the dismantling of the columns, samples taken at different depths were analyzed for solid chemistry and water content. The main results for the latter are presented in Figs. 6 and 7. Water contents in the columns (Fig. 6), except for the BH96–11ox column, range between 15 and 20% after 28 days of drainage. This testifies to an effective drainage of the tailings and to the system effectiveness in simulating a low water table. The BH96–11ox column retains more water than the others. This could be due in part to the water retention capacity of this material that can increase by the presence of precipitates in the solid at the start of the experiment. A sealing problem at the bottom could also be a reason for the bad drainage. This observation (higher water content in BH96–11ox column) mainly explains the lower sulfate production (Figs. 4 and 5) observed for this sample. In fact, saturated materials are less reactive because of the low diffusion of oxygen in the water-filled soil pores. The initial chemical concentrations can be found in Table 1 and corresponds to the grades measured at the bottom of the chemical profiles. Final chemical concentration profiles of sulfide, sulfate, calcium, magnesium, manganese and iron are presented in Fig. 7.

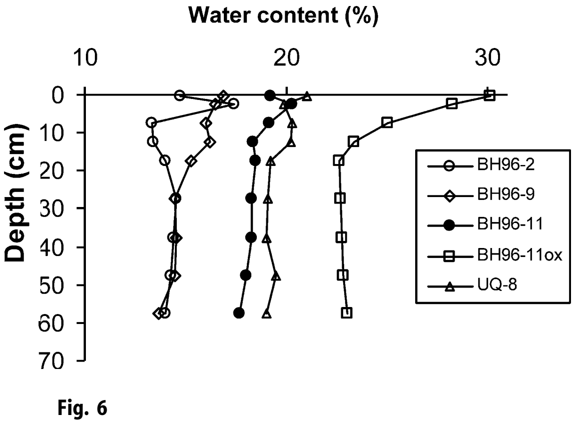


Fig. 6
Water content profiles after column test closure in the five samples studied (30 days drainage)

The sulfide sulfur profile in the column, estimated by the difference between total sulfur and sulfate sulfur, represents the un-oxidized sulfur part. The results show that its concentration seems to decrease slightly at the top of the column, which concurs with the sulfide oxidation process. The sulfate sulfur profile represents the oxidized sulfur part, which precipitated inside the solid sample. It comes mainly from the preliminary oxidation of sulfides prior to experimentation. At the top of the column (first centimeter), the sulfates are strongly dissolved. In the case of the columns BH96–9, UQ-8 and BH96–11, the sulfates seem to precipitate below the oxidized layer, where environment conditions permit it. In the case of the column BH96–2 and BH96–11ox, there is no sulfate precipitation.

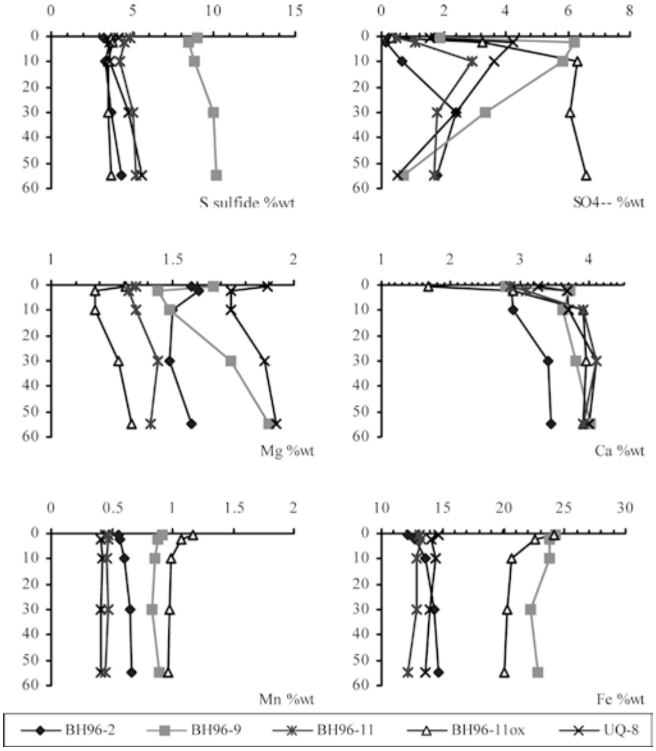


Fig. 7
Chemical profiles (sulfide oxidation—carbonate dissolution) after column test closure in the five samples studied. (Depth in centimeters)

The calcium profile shows that this element is dissolved in the top layer only. The magnesium profile is also presented in the same figure. It seems to dissolve one centimeter below the surface. For Ca and Mg, there is no precipitation evidence within the solid. Their decreased concentration at the top of the column concurs with their dissolution in the neutralization process. The iron profile shows enrichment at the top of the column, except for the BH96–2. This Fe increase confirms the hypothesis of its precipitation made when analyzing the iron-free leachate content in the former section. The profiles corresponding to silicon, aluminum, potassium and sodium (not shown here) show a relative enrichment at the top of the columns due to sulfide and carbonate dissolution. Similar chemical profiles were observed by Blowes and others (1998) at the Joutel mine site. This corroborates the assumption made that column tests reproduce well field conditions.

To study the possible precipitation of secondary phases, mineralogical observations of samples taken during dismantling of the experiment were also made using the SEM imaging coupled with the EDS microanalysis. The images corresponding to the BH96–9 sample (the sulfide rich one) from the top of the column (where precipitation is mostly probable) are presented in Fig. 8. In the SEM backscattered electron image, sulfides appear brighter than the other gangue minerals. The first image series (photos 1, 2 and 3), which represent increasing magnification, shows consolidation of the particles. The fine grains and the fine precipitates formed during the test are probably responsible for the cementation of the coarser particles. This is clearly shown by the secondary electron images photos 4 and 5 and backscattered electron images photos 6 and 7. Photo 7 shows the presence of iron oxi-hydroxides (containing little silicon) and shows secondary gypsum, which is rarely seen in the studied sample. The last images (Photos 8 and 9) show clean pyrite surfaces.

Post testing results: humidity cell tests

As for the columns, the samples were characterized after humidity cell test closure. Water contents measured on the samples coming from humid cells vary between 26 and 28%, except for the BH96–11ox sample which has a higher content of 32%, probably due to the presence of more hydrated and hydroxiled secondary precipitates. Table 4 summarizes the chemical analyses of the five final samples. The main observation is that there is a weak sulfate precipitation. The quantification of the NP depletion gives a remaining NP between 50 and 70% of the initial values as is shown in Table 5. The values listed there represent the main element and NP depletion for the five Joutel samples studied in humidity cells. Depletion represents the remaining proportion. It is often under 100% (which represents the initial state) demonstrating element (as is the case for Ca, Mg, Mn, S) or NP dissolution. When this proportion is higher than 100%, it means a relative enrichment due to the very low solubility of the corresponding element (as Si) and the dissolution of the other elements cited-above. Iron, coming from pyrite oxidation, precipitates for the most part giving near 100% value. The SEM study on the samples after test closure did not give any additional information.

Discussions on the geochemical behavior

Geochemical behavior of the sample tested is examined by representing Eh-pH evolution and by taking the ratio of neutralization elements to oxidation elements (oxidation – neutralization curve). The latter is used to compare and interpret all tests.

Iron and sulfur speciation

The obtained pH and redox potential values were plotted using an iron Eh-pH diagram (Fig. 9). The diagram construction parameters can be found in Lowson (1982). The representation allows an understanding of the pH and Eh variation during the tests and a better understanding of the evolution of iron speciation. All of the pH-Eh projections for both tests are localized in the hydroxide stability field for the tailings studied (Fig. 9). This, as mentioned above, explains the absence of iron in the flushed waters recovered from both kinetic tests. Concerning sulfur speciation, the main occurrence in the flushed solutions is the oxidized form of sulfur corresponding to the measured sulfate. In the test conditions, sulfates cannot precipitate easily and gypsum is near saturation as proven by geochemical modeling using Visual Minteq and the global

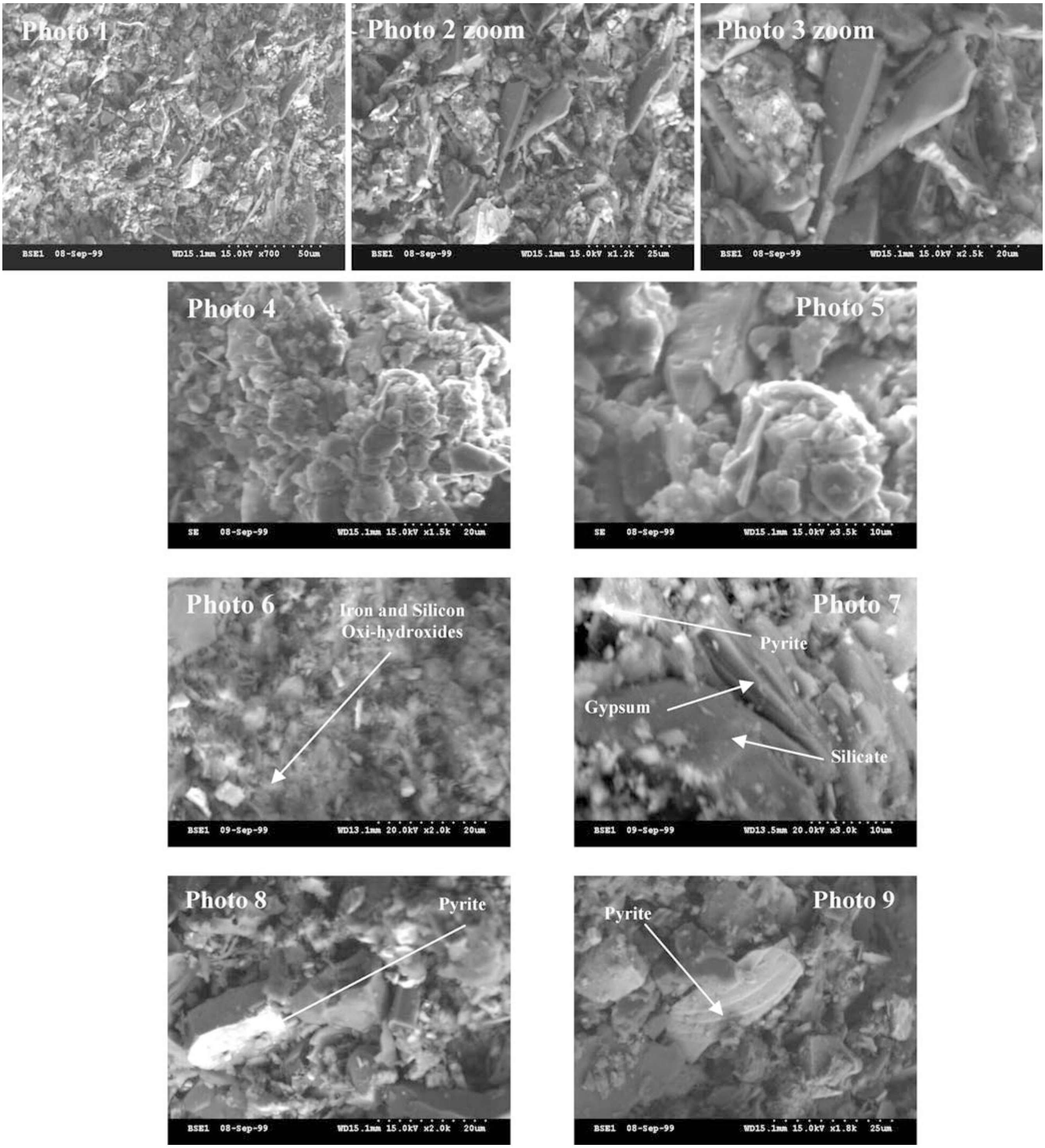


Fig. 8
SEM electron images of the solid sample BH96–9 after test closure

geochemical conditions of the tests (Saturation Index $SI_{\mathrm{gypsum}} = -0.5$).

Oxidation – neutralization curves

This section presents the new approach in interpretation of the acid-generation potential of tailings using results from kinetic tests. The species used are sulfates that represent the main oxidation product and the sum of Ca + Mg + Mn, which represents the main carbonate dissolution products. The cumulative mass of sulfates measured in the flushed waters is plotted versus the cumulative amount of calcium, magnesium and manganese. These cumulative concentrations are corrected for the recovered volume and normalized to one kilogram of solid tailings. The oxidation–neutralization curve represents the geochemical evolution of the acid to neutralizing element-produced ratios during kinetic tests. The obtained

Table 4
Chemical analyses and static test results of the five samples tested in humidity cell (after dismantling)

	BH96–2	BH96–9	BH96–11	BH96–11 ox	UQ-8
Al (Wt%)	4.9	2.32	5.05	3.05	4.81
Ba (µm/g)	220	66	90	120	130
Ca (Wt%)	3.05	3.4	4.12	3.47	4.27
Cd (µm/g)	<2	<2	<5	<2	<2
Cu (µm/g)	14	25	0	12	66
Fe (Wt%)	14.5	23	13.2	21.4	15
K (Wt%)	0.41	0.22	0	0.37	0.51
Mg (Wt%)	1.58	1.62	1.29	1.27	1.84
Mn (Wt%)	0.66	0.848	0.495	1.03	0.448
Na (Wt%)	2.47	0.87	2	1.28	1.94
S (Wt%)	4.02	10.2	4.92	5.16	5.14
SO_4^- (Wt%)	0.24	2.05	0.538	5.2	1.5
Si (Wt%)	16.91	11.88	21	12.74	17.28
Zn (µm/g)	102	125	0	96	119
Ca/Mg	1.9	2.1	3.2	2.7	2.3
PN kg $CaCO_3$/t	88.2	83	100	61.5	108
PA kg $CaCO_3$/t	123.1	297.1	148.1	106.3	144.8
PNN net kg $CaCO_3$/t	−34.9	−214.1	−48.1	−44.8	−36.8

curves, which are called oxidation – neutralization curves are given in Fig. 10. The Joutel tailings give a linear shape oxidation–neutralization curve for column tests and humidity cell tests. Slopes (a) and correlation coefficient (r) from linear regression made on each curve are given in Table 6. Correlation indices are very high showing a linear behavior. The slope values vary between 0.33 and 0.41. They are, for all tailing samples, higher in the case of the humidity cell in comparison to the column tests. No evidence explains the small difference in terms of slope value between the samples. The explanation may take into account the differences in terms of chemistry and specific surface of the samples and the test reproducibility (void ratio, permeability, etc.).

The oxidation – neutralization curve can be used as a valuable criterion to evaluate and predict the geochemical behavior of any tailings. For near-neutral tailings that show little or no precipitation of the elements concerned it can be possible to predict the acidity potential, under certain hypothesis, by extrapolating the oxidation–neutralization curves and by projecting the initial sulfate (converted from sulfur content) and Ca, Mg and Mn concentrations of the tailings. Figure 11 shows this representation for the five samples studied. The hypothesis underlying this method of interpretation is that the geochemical environment stays the same, the ratio between the neutralizing and oxidation products stays linear, and that mineralogy will not affect linearity of the relation in the long term (ex. depletion of a mineral or precipitation). These hypotheses are interdependent. They can be considered realistic as long as conditions (pH, Eh, temperature) remain the same. For the Joutel tailings it is permitted to use this interpretation method considering that the BH96–11ox sample has a similar behavior as the unoxidized (fresh) sample that can be seen in the plotted curves, even if the material was exposed to climatic conditions for more than 20 years.

Table 5
Main elements and NP's depletion corresponding to the five samples tested in humidity cell (after dismantling)

Depletion (%)	BH96–2	BH96–9	BH96–11	BH96–11 ox	UQ-8
Ca	78.4	78.3	95.6	78.9	86.3
Mg	89.8	83.1	81.6	92.0	87.2
Mn	93.0	91.2	103.1	88.0	95.3
S	84.1	96.2	77.4	80.2	85.8
Fe	96.0	99.1	103.1	96.8	98.0
Si	138.6	113.1	151.1	111.8	112.2
AP	90.3	92.9	76.5	87.9	73.9
NP	73.5	55.3	66.7	53.5	60

The curve extrapolation allows the evaluation of the AGP potential of the studied samples. The sample will generate acid if carbonates are depleted while sulfides are still available (in this case, the sample will be projected under the oxidation – neutralization curve). If the sample is not acid generating, it contains carbonates in sufficient amount to neutralize all acid generated by sulfide oxidation (in this case, the sample will be projected over the oxidation – neutralization curve). Among the studied samples, only BH96–9 is under its curve classifying it as acid generating. The sample BH96–11 is at the limit of acid generation. The other samples would not generate any acid.

Figure 11 can also be viewed as the NP/AP graphic for interpretation of static tests, with the non-acid generating, the uncertain and the acid-generating zones. The uncertain zone defined by the kinetic test represents the zone between the neutralization curve having the highest slope (0.41) and the lowest slope (0.33). To this can be added a security margin called "Security field of the kinetic test" (slopes between 0.45 and 0.41) as shown in Fig. 12. Samples coming from the Joutel site which plot over the 0.45 slope are considered non-acid generating. This zone (between 0.33 and 0.45) can be compared to the uncertain zone used by the static test (NP/AP between 1 and 2). Some samples that are acid generating according the static test classification (e.g. BH96–2 and BH96–11) are actually non-acid generating or in the uncertain zone defined by

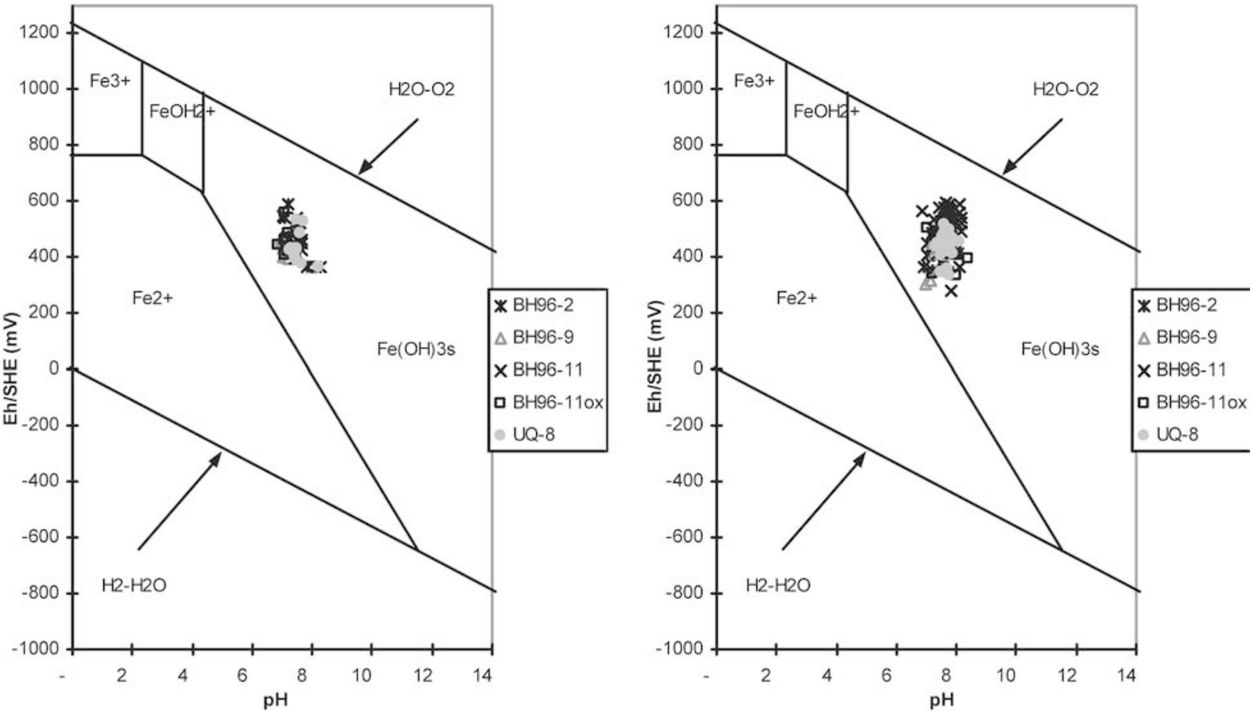


Fig. 9
Eh and pH projection into the iron species Eh-pH diagram for Joutel tailings (*left*: column tests, *right*: humidity cell tests)

the kinetic test. Thus, kinetic testing allowed the prediction of the potential of acid generation of the Joutel samples and to predict the uncertainty zone of the static test for these tailings, based on the previously mentioned hypothesis and knowing that the samples studied are representative of the heterogeneity of the Joutel tailings pond.

Kinetic tests comparison

This section compares results obtained from both kinetic tests. The oxidation–neutralization curves presented in the previous section are plotted for each sample in Fig. 13. One can see that for the column tests the accumulation of elements in solution is less than for the humidity cell tests. This is true for all the samples studied, even if the duration of the column test is longer than that of the humidity cell test (405 to 445 days for the column test compared to 210 days for the humidity cell test, except for the extended test done on sample BH96–11 which lasted 378 days). This can be explained by differences in the experimental procedures of the two tests: the amount of solid used (750 g versus 8,300 g, respectively, for the humidity cell and column); the surface area exposed to air (308 cm^2 versus 157 cm^2, respectively, for the humidity cell and column); the frequency of flushes (1 month for columns versus 1 week for humidity cell) and the severity of the test cycles.

The difference between the two kinds of tests is well seen in Fig. 14 which presents depletion curves for the five samples. On the right of Fig. 14, one can see another way of expressing acid-generation potential evolution. There is a reduction of sulfate production attesting to a slowing of sulfide oxidation, more apparent particularly for sample BH96–11. This phenomenon has been observed before in

Fig. 10
Neutralization curves corresponding to kinetic tests performed on the five Joutel tailings (*left*: column tests, *right*: humidity cell tests)

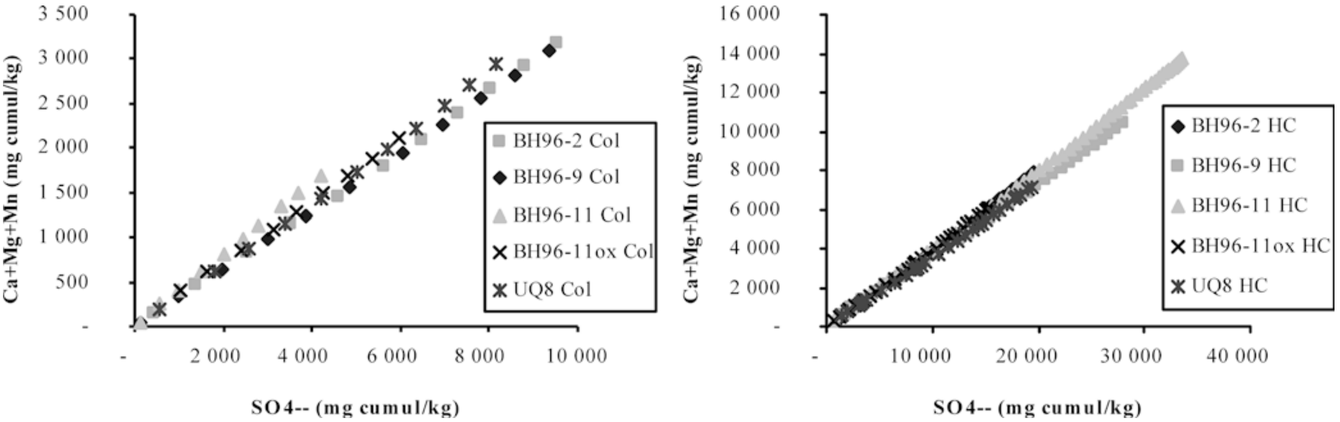


Table 6
Oxidation–neutralization slope values for the five samples studied

	Column tests		Humidity cell tests	
Samples	a	r	a	r
BH96–2	0.33	0.9994	0.41	0.9997
BH96–9	0.33	0.9998	0.37	0.9996
BH96–11	0.40	0.9998	0.41	0.9996
BH96–11ox	0.34	0.9997	0.40	0.9998
UQ-8	0.36	0.9994	0.37	0.9995

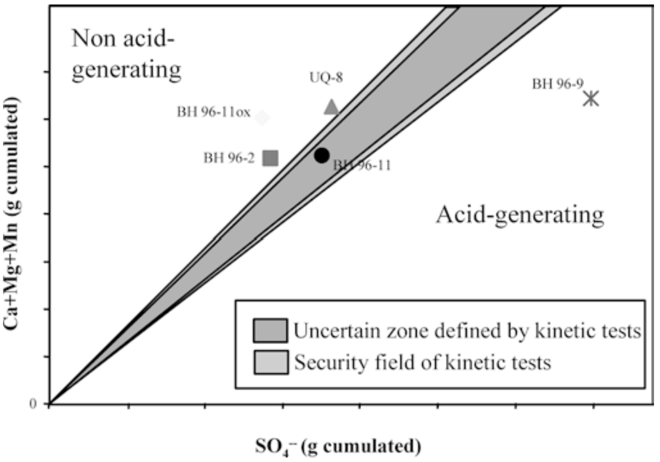


Fig. 12
Position of the Joutel samples in regard to the kinetic test criterion

the literature and described by many authors (Scharer and others 1991; Cruz and others 2001). It can be explained by at least two mechanisms: the first one is surface coating due to precipitation of secondary phases from the pore waters charged in metals (here it is mainly iron explaining its absence from the flushed waters recovered for both test types), the second one is fine particle disappearance due to their total oxidation knowing that they generally oxidize faster than the coarser ones. Moreover, Fig. 14 (left) shows the comparison between the depletion of the sulfide content (converted to sulfate in the remaining percentage) as a function of the depletion of carbonates (expressed as the summation of Ca + Mg + Mn converted in the remaining percentage) for column and humidity cell tests. Results from column tests show that the oxidized sulfide portion and the carbonates, having neutralized the acidity, represent only a third of what was depleted in the humidity cells.

Although cumulative elements recovered for both test types are different, Figs. 10, 13 and 14 show that the ratio between neutralizing and oxidation products is similar. This similarity is apparent between test type and between samples studied. Studied sample in this project have similar oxidation–neutralization curves for both types of kinetic test, the only exception being sample BH96-2 where the column test seems to produce less neutralizing (or more oxidation). Slope values confirm the similarity observed between each type of test for this method of interpretation. Values vary between 0.33 and 0.40. It is important to note that the difference between the slope of samples studied BH96–11 and its corresponding oxidized material BH96–11ox is small.

Conclusions

The two main objectives of this study were: (1) to evaluate the acid-generation potential of the Joutel tailings pond by the use of kinetic tests, and (2) to compare the two types of kinetic tests: the column and humidity cell test.

Five samples chosen to represent the heterogeneity of the Joutel tailings pond were tested for up to 400 days. Geochemical results from both kinetic tests gave a stable pH around 7 and Eh values between 450 and 500 mV. Most of the acid neutralization came from the dissolution of carbonates. Post-testing results and chemical modeling show that except for iron oxi-hydroxides, there was no significant precipitation of species.

Oxidation–neutralization curves were established for all tests using the ratio between Ca, Mg, Mn release (carbonates dissolution) and sulfates production (oxidation). They were

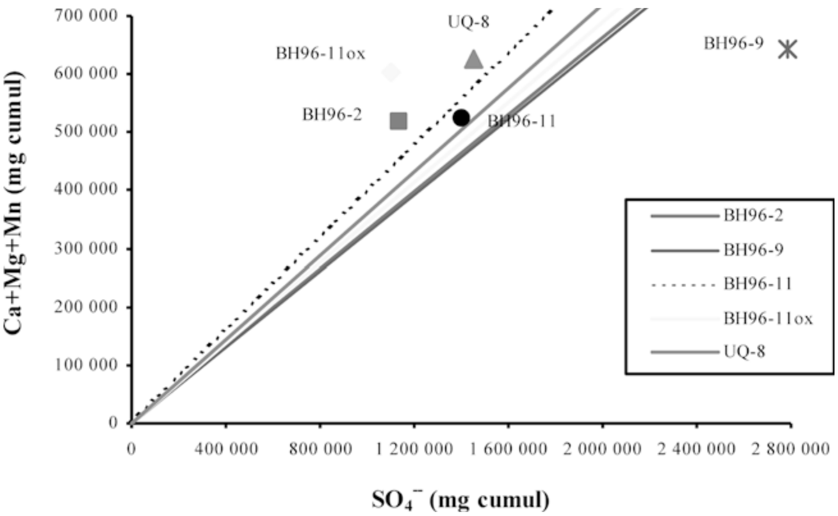


Fig. 11
Extrapolation of the neutralization curves and projection of Joutel tailing initial compositions

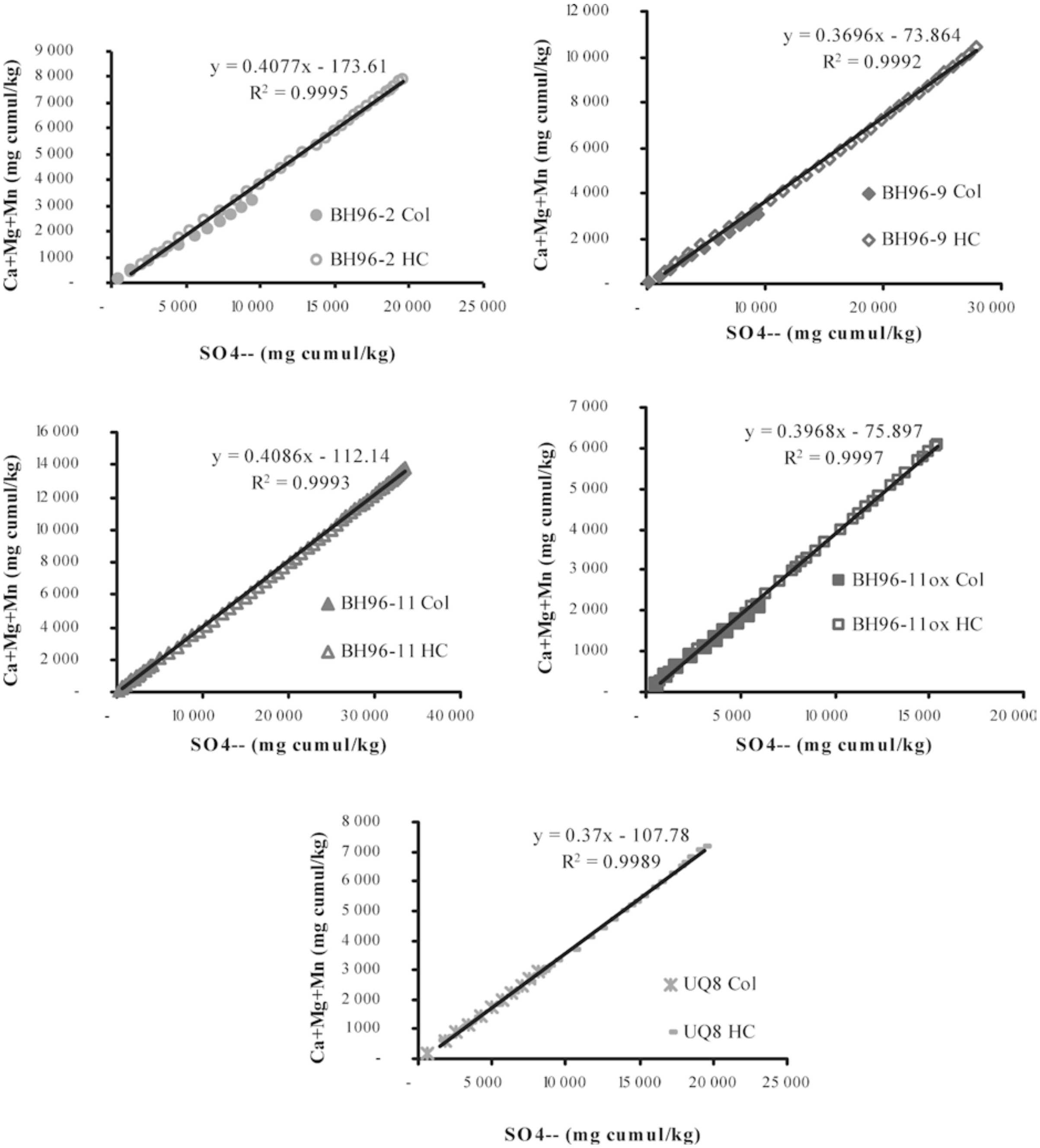


Fig. 13
Comparison between the oxidation–neutralization curves of the two test types, for the five studied samples

used to determine the acid-generation potential of the samples based on certain assumptions. If initial concentration in SO_4 and the sum of Ca, Mg and Mn of samples is located over the oxidation – neutralization curve, they are considered as non acid generating. If the point is located underneath, the tailings are considered as acid generating. By using this approach, samples BH96–11ox, UQ-8 and BH96–2 are classified as non acid-generating, samples BH96–9 and BH96–11 are acid generating, and sample BH96–11 is very close to its corresponding line.

The assumptions for this method of interpretation are that the geochemical environment stays the same, the ratio between neutralizing and oxidation products stays linear, and that mineralogy does not affect linearity of the relation in the long term in the case of Joutel tailings. This is confirmed by results obtained from sample BH96–11ox that are similar to the ones from BH96–11, its unoxidized counterpart. This method of interpretation works well with low sulfide tailings, and test conditions where precipitation of the studied species is minimal.

Comparison between humidity cell tests and column tests has also been done using the oxidation–neutralization curve interpretation method. The results clearly showed that although the cumulative elements recovered from solution are different for humidity cells and columns due to experimental conditions, the curves representing the ratio of neutralizing elements to oxidizing products are

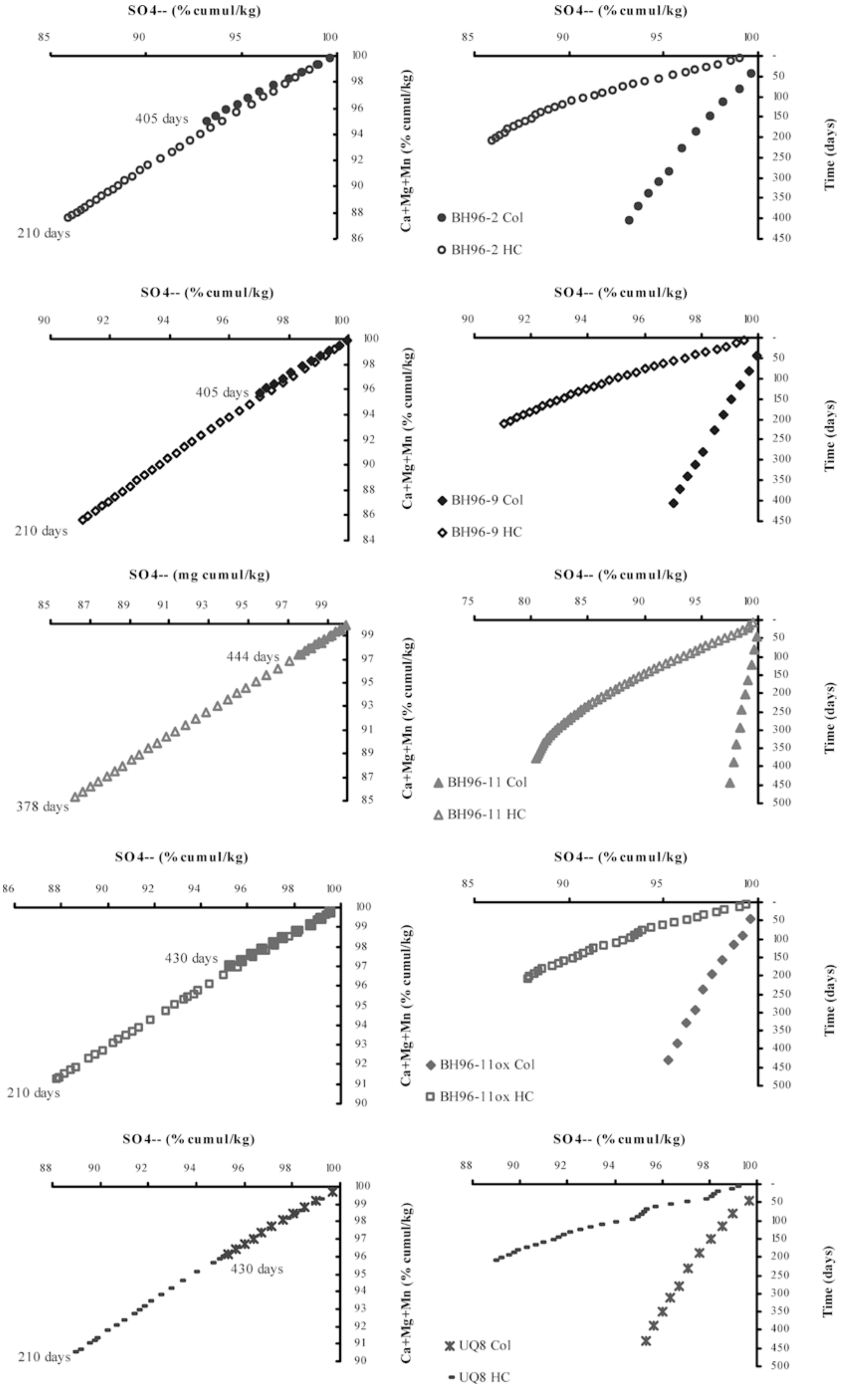


Fig. 14
Comparison between sulfide (sulfates converted) and carbonates (Ca + Mg + Mn) depletion curves (*left*) and sulfide (sulfates converted) depletion curve as a function of time (*right*) for the two types of tests done on the five samples studied

similar for both types of tests on Joutel tailing samples even if the humidity cell is more aggressive.

Finally, it can be postulated that column tests are more adapted for the prediction of water quality corresponding to a given tailings impoundment. However, for the determination of the acid-generation potential at mid and long terms, humidity cell tests are more advised.

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