High Temperature Oxidation (Heating) of Sulfidic Paste Backfill: A Mineralogical and Chemical Perspective

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Abstract

Paste backfill is becoming widely used in modern mining operations worldwide. Benefits of implementing the paste backfill technology are associated with improved mining operation and better environmental management. However, under certain circumstances, paste backfill may be affected by high temperature oxidation either through self-heating mechanisms or by an external heat source. In such cases, mine production may have to be interrupted because of potential SO_2 hazards, which may ultimately lead to loss of ores if a stope has to be sealed off permanently. The risk of fatalities exists if large quantities of SO_2 are emitted into the air. This paper describes studies in which specimens of oxidized paste backfill sampled underground at three different mines were investigated to outline the chemical and mineralogical changes that occurred during the oxidation and to verify if self-heating was involved. These investigations allowed us to suggest an oxidation sequence with increasing temperatures. The oxidized paste specimens seem to have derived from the original paste via a series of oxidation, neutralization, dehydration and mineralogical transformation reactions taking place at increasing temperature ranges. The less oxidized, green-greyish paste reacted at temperatures less than 100 °C and did not emit SO_2. The more oxidized, orange to red paste reached the temperature range of 250-400 °C and emitted SO_2 during its oxidation process. The color of the red paste specimen reflects the pigmentation by hematite (red). During the heating event, gypsum is transformed into anhydrite. Base on the findings, various preventative, monitoring and corrective measures can be taken to reduce the risk of heating of paste and emission of toxic SO_2.

Introduction

The implementation of paste backfill technology in modern metal mining operations must take into account the physical and chemical stability of the paste mixture sent underground, which may vary with time. In addition, the possibility of self-heating of the high-sulfide tailings used in the paste backfill (Moerman et al., 1999) must be addressed. The potential for self-heating in concentrate due to sulfide oxidation is well documented (Rosenblum et al., 2001) and is of concern during ore concentrate transportation. Similarly, mine operators have to be aware of the possibility of paste backfill heating (either self-heating, or heating derived from another source such as reactive muck) which may represent underground health and fire hazards. This may be the case if a backfilled stope collapses permitting large amounts of air to access reactive moist paste. In such cases, mine production may have to be interrupted because of potential SO_2 hazards, which could ultimately lead to loss of ores if a stope has to be sealed off permanently. The risk of fatalities exists if large quantities of SO_2 are emitted into the air.

This paper presents the results of three case history investigations where highly oxidized paste backfill specimens were recovered underground at two mines in northern Quebec (A, B) and one mine in New Brunswick (C).

Case Study Mine A

The problem of suspected paste fill self-heating and SO_2 emission has been observed twice at Mine A in northern Quebec. The first event occurred during May 1998 in a stope and the second event occurred in a different stope during February 1999. At that time, Mine A has been operating underground paste backfill for four years.

After the first event occurred, fragments of strongly oxidized (yellow and red) paste backfill were found underground and suspected to be a source of SO_2 emission detected earlier.

Three paste backfill specimens (Figure 1A to C), one unaltered (grey color) and two strongly oxidized (one yellow and the other red) were analyzed for whole-rock chemistry, mineralogy, SEM, ABA, sulfur and sulfide speciation. The main objective was to reveal the oxidation and SO_2 production mechanisms and conditions that produced the yellow and the red paste specimens.

The two fragments of heavily oxidized paste backfill were retrieved in 1998 from underground near other oxidized muck and waste rock materials. It was suggested that these fragments have broken away from the bulk paste backfill because of a failure and have been oxidized "ex-situ".

A typical unaltered paste sample is olive gray in color (MA-F) and a few air voids less than 5 mm in size are visible (Figure 1A). The powdered sample reacted mildly with dilute HCl (10%), indicating the presence of carbonates. The main minerals are quartz, chlorite, albite, pyrite, ankerite with minor siderite, pyrrhotite chalcopyrite, sphalerite, ilmenite and magnetite.

The first type of oxidized paste is much harder than the unaltered paste and has a yellow-brown color (MA-Y). The sample is characterized by the presence of a 3-cm thick zone of disseminated white clusters at the periphery of the sample (Figure 1B). The white clusters are generally less than 5 mm in size. The powdered sample reacted only slightly with dilute HCl.

The second type of oxidized paste sample is red in color (MA-R) and shows zoning in coloration from yellow brown to orange to red from the outside to the inside. It is characterized by numerous white clusters disseminated throughout the sample, except at its margin (Figure 1C). The white clusters are larger in size (up to 10 mm) than those observed in Type 1 oxidized paste. The sample shows fractures in both the radial and transverse directions, which may suggest that the sample underwent expansion. The powdered sample did not react with dilute HCl.

The degree of oxidation is quite surprising, as paste backfill is normally considered non-reactive due to its low permeability to oxygen and alkaline pH. Furthermore, a previous study of mine A tailings showed low level of self-heating (5.72°C/h) that should not pose a problem when used as paste backfill. The unaltered paste indicates an even lower self-heating potential of about 1°C/h.

Case Study Mine B

At a polymetallic mine site in northern Quebec, red and green-grey colored paste backfill lumps about the size of a fist were found underground in ore muck piles in a stope in May 2001. Out of concerns of self-heating problems and potential SO_2 hazards, these oxidized paste backfill specimens were sent to NTC for analysis. The two oxidized specimens were found in the same stope and no elevated SO_2 was detected at the site's air quality monitoring stations.

The less oxidized fragment (MB-G) is grey-greenish in color, round in shape, and measures about 15 cm in diameter. On this specimen only local spots of heavy oxidation were seen, showing a yellowish to orange coloration (Figure 1D). The more oxidized specimen (MB-R) is red in color and ball-shaped, measures about 7 cm in diameter, and has been altered throughout (Figure 1 E, F). Both fragments were submitted for analysis with a sample of fresh filter cake taken from the paste plant (MB-Tails) for comparison.

Mineralogical analysis indicates that the dominant primary minerals in the fresh tailings and less altered paste are quartz, chlorite, talc, sepiolite, pyrite, calcite, ankerite, magnetite and pyrrhotite. The mineralogical contrasts of the less altered green (MB-G) and the more altered red (MB-R) paste specimens provide hints toward the conditions of their formation. In comparison with the green paste, the main mineralogy changes observed in the red paste are: 1) nearly complete depletion of carbonates and pyrrhotite, 2) appearance of gypsum, goethite, anhydrite, and hematite. In contrast only gypsum is observed as secondary minerals in the less altered paste.

Case Study Mine C

In 2001, an underground muck heating event occurred at base metal mine C accompanied by

emission of sulfur dioxide (SO_2). Following the event, three types of oxidized specimens were handpicked for post-mortem analysis. These specimens are described as hot paste (grey in color), hot glowing paste (orange in color), and red lumps in ore pass (red interior color). The hand specimens were analyzed in detail for chemical, physical, mineralogical, and self-heating properties.

The grey paste fill specimens (Figure 1G) were hot to the touch at the time of sampling. The orange paste fill specimens (Figure 1H) were glowing hot at the time of pick up. Both the above two types of specimens were air cooled. Small piece of red, paste-like material (usually less than an inch in diameter) were found scattered around the ore pass entrance where the water-cooled hot muck was dumped. These pellet-like specimens (Figure 1I) were picked up as specimens. They were very hard to break and appeared completely oxidized from the outside to the core.

The main minerals present in the two altered paste specimens are quartz, chlorite, pyrite, calcite, ankerite, gypsum and pyrrhotite. The mineralogical contrasts of the less altered grey (MC-A), the more altered orange (MC-B), and the most altered red (MC-RL) specimens provide hints toward the conditions of their formation. In comparison with the grey paste specimen (MC-A), the main mineralogical changes observed in the red lumps (MC-RL) are: 1) nearly complete depletion of carbonates and pyrrhotite, and 2) appearance of anhydrite and hematite. The orange paste specimen (MC-B) shows mineralogy that is somewhere between the grey paste and red lump specimens.

Results of Mines A B C Investigations

An acid base accounting (ABA) was performed on the mines A, B and C paste samples and the results are shown in Tables 1, 2 and 3. Acid base accounting (ABA) is an analysis to characterize the material's potential to generate sulfuric acid through oxidation.

The progression of sulfide (pyrite) oxidation and the neutralization of the acid produced from the unaltered to the more oxidized paste samples (yellow) to the red specimens is strongly evidenced by the compositional changes in paste pH, $Fe_{sulfides}$ and S^{2-}, SO_4, and CO_2 (Tables 1 to 3).

Table 1. Mine A fresh and oxidized pastes ABA.

MineA	MA-F	MA-Y	MA-R
	Fresh paste	Yellow paste	Red paste
Paste pH	7.91	2.93	2.33
$Fe_{sulfides}$	11.81	6.50	4.08
S total	14.00	12.40	11.90
SO_4	1.02	14.45	21.40
CO_2	5.32	1.21	0.29
S2-	13.66	7.58	4.77
SAP	426.88	236.98	148.96
CNP	120.64	27.44	6.58
CNNP	-306.24	-209.54	-142.38
CNP/SAP	0.28	0.12	0.04

SAP= Sulfides Acid Potential, CNP=Carbonate Neutralization Potential, CNNP= Carbonate Net Neutralization Potential. Expressed in kg $CaCO_3$ equivalent per tonne of sample.

Oxidation of pyrite caused both $Fe_{sulfides}$ and S^{2-} to decrease and SO_4 (the oxidation product) to increase, whereas neutralization by carbonate of the sulfuric acid generated as a result of pyrite oxidation is strongly indicated by the decrease in CO_2 content. The paste pH recorded in the oxidized paste samples is much lower than that in the unaltered paste or least altered equivalent, indicating that the yellow and the red specimen had become net acid-producing (Figure 2).

Table 2. Mine B tailings and oxidized pastes ABA.

Mine B	MB-tails	MB-G	MB-R
Sample	Filter cake	Green paste	Red paste
Paste pH	8.09	5.58	4.16
$Fe_{sulfides}$	11.04	6.11	1.63
S total	17.99	13.10	12.71
SO_4	0.90	8.12	17.73
CO_2	8.31	4.64	0.41
S^{2-}	13.57	7.56	2.52
SAP	424.06	236.25	78.75
CNP	188.44	105.22	9.30
CNNP	-235.62	-131.03	-69.45
CNP/SAP	0.44	0.45	0.12

Legend as in Table 1.

All three mines' paste samples have high sulfide acid potential (Mine A: SAP= 149-427 kg

$CaCO_3$ eq./t; Mine B: SAP= 79-424 kg $CaCO_3$ eq./t; Mine C: SAP= 129 – 981 kg $CaCO_3$ eq./t), indicating that there is still some sulfides remaining for further oxidation.

Table 3. Mine C oxidized pastes ABA.

Mine C	MC-A	MC-B	MC-RL
Sample	Hot paste not glowing	Hot paste glowing	Red lump in ore pass
Paste pH	9.35	3.65	2.13
$Fe_{sulfides}$	28.17	21.50	2.76
S total	31.80	29.40	11.60
SO_4	1.14	14.30	22.40
CO_2	5.23	1.53	0.77
S^{2-}	31.40	24.60	4.12
SAP	981.25	768.75	128.75
CNP	118.59	34.62	17.56
CNNP	-862.66	-734.13	-111.19
CNP/SAP	0.12	0.045	0.14

Legend as in Table 1.

The amount of SO_4 increased drastically in the more oxidized paste specimens (Mine A: yellow paste SO_4=14.45%, red paste SO_4=21.40%; Mine B: green paste SO_4=8.12%, red paste SO_4=17.73%; Mine C: orange paste SO_4=14.30%, red lumps SO_4=22.40%) relative to the unaltered paste specimen (Mine A: 1.02 % SO_4; Mine B: 0.90 % SO_4; Mine C: 1.14 % SO_4). This increase in SO_4 is a direct result of sulfide oxidation and reflects sulfate formation as secondary minerals from acid neutralization by Ca-bearing carbonates (calcite, ankerite, dolomite).

The carbonate neutralization potential (CNP) is fairly low for the most oxidized paste samples (Mine A: 7 and 27 kg $CaCO_3$/t; Mine B: 9 and 105 kg $CaCO_3$/t; Mine C: 17.6 and 35.0 kg $CaCO_3$/t) compared with the unaltered paste (Mine A: 121 kg $CaCO_3$/t; Mine B: 188.4 kg $CaCO_3$/t; Mine C: 121 kg $CaCO_3$/t), indicating a depletion of carbonate minerals with degree of oxidation (CO_2 decreasing)

The carbonate net neutralization potentials are negative (more so in the unaltered than the oxidized specimen), indicating further potential for net acid generation, as is also reflected by the low CNP/SAP ratios.

The Interpretation of the data indicates that the most oxidized paste specimens (yellow to orange and red in color) had undergone extensive oxidation and become net acid-generating. Despite their colors, the sulfides in these specimens are not completely depleted.

The possible causes of high temperature oxidation and reactions mechanisms are discussed in the following sections.

Reaction Routes as a Function of Temperature

The mineralogical changes in the three case studies presented are very important in deciphering the oxidation routes and events leading to the final pastes chemistry.

The temperature to which a paste material is subjected may have profound effects on the chemical and physical properties of the paste. When heated, a paste material may emit SO_2, expand or shrink, dehydrate, spall and crack, etc. These phenomena can cause loss of physical strength and integrity in the paste backfill, contribute to environmental pollution, or create health and safety hazards to underground miners. Several of these aspects are discussed in more detail below.

Formation and breakdown of sulfates

Three calcium sulfate minerals are often encountered; two are stable phases - gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), whereas one is metastable - bassanite ($CaSO_4$ $0.5H_2O$).

Gypsum can be present in a paste backfill as a primary constituent of the tailings or as an added component in the cement. Gypsum can also be formed during the low-temperature oxidation of sulfides as a product of neutralization of the sulfuric acid produced. Bassanite and anhydrite can formed from dehydration of gypsum when heated. Bassanite starts to form at 70°C when gypsum looses 75% of its crystalline water:

$$CaSO_4\ 2H_2O = CaSO_4\ 0.5H_2O + 1.5\ H_2O$$

When the temperature reaches 100°C, bassanite is transformed to anhydrite:

$$CaSO_4\ 0.5H_2O = CaSO_4 + 0.5\ H_2O$$

Thus, presence of bassanite in a sample indicates that it was once subjected to a temperature between 70-100°C whereas the presence of anhydrite suggests it has experienced a temperature in the range of 100-200°C. Figure 3 shows SEM photos of secondary sulfates formed during high temperature oxidation of paste fill at Mines A to C.

Primary ettringite formation (PEF) occurs during early hydration of Portland cement in a reaction involving tri-calcium aluminate ($Ca_3Al_2O_6$), water and gypsum:

$$Ca_3Al_2O_6 + 3\ CaSO_4{\cdot}2H_2O + 26\ H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$$

Secondary ettringite can also form in a paste backfill as a result of sulfate attack (Bernier et al., 1999). In response to a temperature increase, ettringite will break down to monosulfate and portlandite at about 120 °C.

Formation of Goethite and Hematite

Iron hydroxides and oxides such as goethite (FeOOH) and hematite (Fe_2O_3) can form during sulphide oxidation. Both minerals are strong pigments that give either a yellow (goethite) or a red (hematite) color to the material containing them. Goethite is stable below 250°C. In the range 250-350°C, goethite dehydrates to form hematite and water (Dekkers, 1988):

$$2\ FeO(OH) = Fe_2O_3 + H_2O$$

Because goethite is present in the yellow paste specimen, we can assert that the oxidation temperature was below 250°C. In contrast, the red specimen contains hematite, indicating an oxidation temperature above 350°C.

SO_2 Emission

If pyrrhotite is present and gets oxidized, elemental sulfur can be produced in the temperature range 100-150°C. This reaction produce elemental sulfur that will oxidize into SO_2 in the presence of oxygen. If only pyrite is present, the paste has to be heated to a temperature greater than 350°C before pyrite undergo oxidation with concurrent SO_2 emission.

Take the example of pyrite, between 350 and 400°C, pyrite oxidizes to ferrous sulfate and SO_2:

$$FeS_2 + 3\ O_2 = FeSO_4 + SO_2$$

If the temperature exceeds about 400°C, pyrite is further oxidized to hematite (Fe_2O_3) and SO_2:

$$2\ FeS_2 + 5.5\ O_2 = Fe_2O_3 + 2\ SO_2$$

The number of moles of SO_2 per mole of pyrite oxidized is one for both reactions.

SO_2 toxicity

A detailed listing of potential effects of occupational exposure to sulfur dioxide upon human health has been presented in an NIOSH internal report (Baier, 1977). The main symptoms occurring upon exposure to various SO_2 concentrations have been summarized by UK Air Accidents investigation Branch (UKAAIB, 1985) and are reproduced in Table 4.

Table 4 Response of Humans to various concentrations of SO_2.

SO_2 ppm	**Symptoms**
3-5	Odour threshold
5	Threshold limit value (TLV)
8-12	Slight irritation of eyes and throat
20	Coughing and eye irritation
30	Immediate strong irritation, remains very unpleasant
100-250	Dangerous to life
>600	Death in a few minutes

Miners are not typically reported as being at risk in their day to day routines as would be workers in a smelter. However, safety procedure at a mine site should include dealing with paste backfill heating as a potential risk for human health and underground fire hazard.

<u>Source of Heat</u>

The oxidation temperature was inferred from the mineralogy of the paste specimens as being up to 100 °C for the grey paste specimen and > 400 °C for the orange paste and the red paste specimens analyzed at mines A, B and C. The increased oxidation temperatures that may lead

to SO2 emission and fire hazard according to the reaction mechanisms describe previously necessitates a source of heat. There are a few potential heat sources in an underground environment, as listed below:

- failed paste itself containing high pyrrhotite and other sulfides,
- self-heating of development waste rocks piled underground (higher pyrrhotite and pyrite),
- Heat (and high pressure) given off by blasting
- Other human-related causes which are difficult to identify.

The external heat source hypothesis requires the ex-situ paste material (the specimens) to be placed near or in contact with the heat source.

Discussion and Conclusion

The reaction mechanisms presented previously provide hints to the oxidation temperature that prevailed for the oxidized paste specimens. The mineralogical changes at different oxidation temperatures are summarized in Table 5.

We can postulate a sequence of mineralogical changes with increasing temperature. The formation of gypsum and goethite would have occurred at an oxidation temperature below 100°C to produce Type 1 oxidation represented by the yellow to orange paste specimens at mines A, B and C. At this temperature, no SO_2 would have been released to the atmosphere. In the presence of pyrrhotite in the pastefill, SO_2 could have been emitted upon elemental sulfur oxidation. A higher oxidation temperature (>250°C) is inferred to explain the formation of anhydrite and hematite in Type 2 oxidation represented by the red paste specimens. If the temperature was greater than 350°C, SO_2 emission would have occurred from pyrite oxidation. The dehydration reactions would have resulted in a volume loss, creating a differential stress that would have favored cracking. Cracking is indeed observed on the red specimen at mine A as circular and transversal fractures.

A puzzling fact is the presence of hydrous sulfates (in the white clusters of) amongst the anhydrite in the red specimen. The most probable explanation is a reversion of anhydrite to hydrated sulfates under the influence of moisture after the heating of the specimen had ended, in a similar way to secondary ettringite formation in high temperature cured concrete.

Mineralogy of the paste specimens can be used as a post-mortem "thermometer" indicator of the maximum temperature the paste has oxidized at. This is because mineralogical transformations occur at certain temperature ranges, and information about the presence and lack of certain minerals in the paste specimens can be used to deduce the oxidation temperature.

Unfortunately, we do not have sufficient evidence to make a definite conclusion about the source of the heat for the three case studies reviewed in this paper. The cause of the temperature rise could be self-heating of high-pyrrhotite failed paste itself or external heat sources. This is a common situation in most mines where heating events are known to have taken place. That is, heating event is not a result of designed experiments, but rather ad hoc events. Only post-mortem analysis can be conducted, which is often insufficient to determine a cause-effect relationship.

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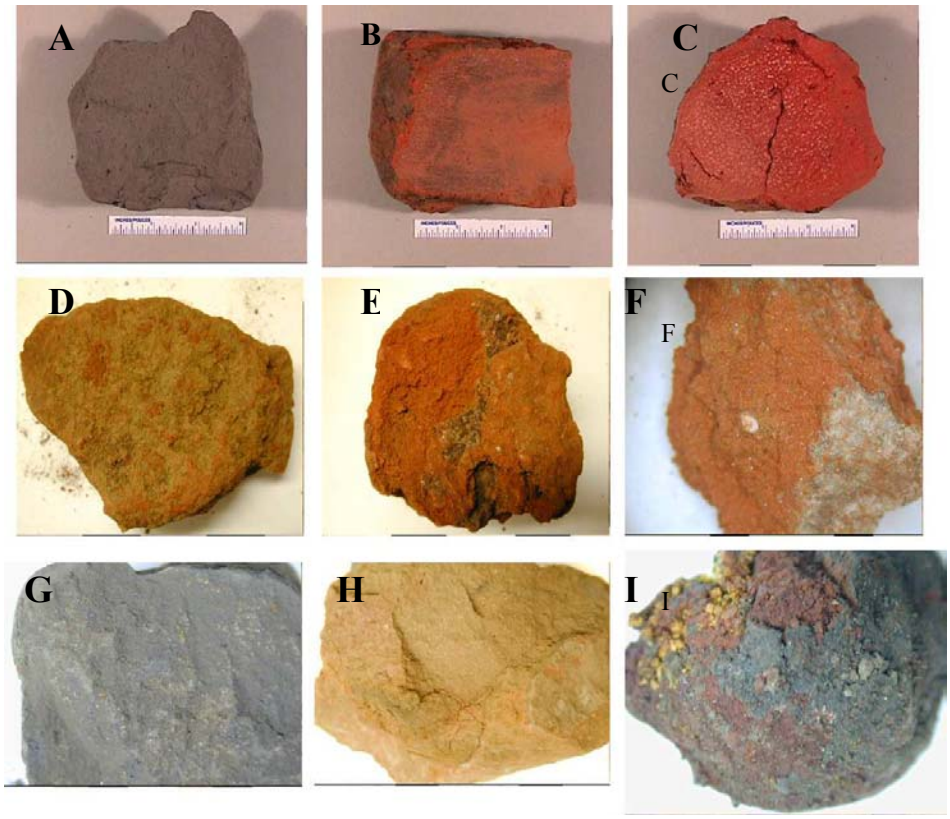

Figure 1 Photographs of fresh and heated paste from the 3 mine sites. **Mine A:** A) Fresh paste (olive grey, MA-F), B) first type oxidized paste (yellow-brown, MA-Y), C) second type oxidized paste (red, MA-R) with white clusters; **Mine B:** D) least oxidized paste (grey-greenish, MB-G), E-F) most oxidized paste specimen (orange-red, MB-R), notice the large white cluster in the red matrix; **Mine C:** G) less altered grey paste (MC-A), H) more oxidized paste (orange, MC-B), I) most altered paste (red lumps, MC-RL)

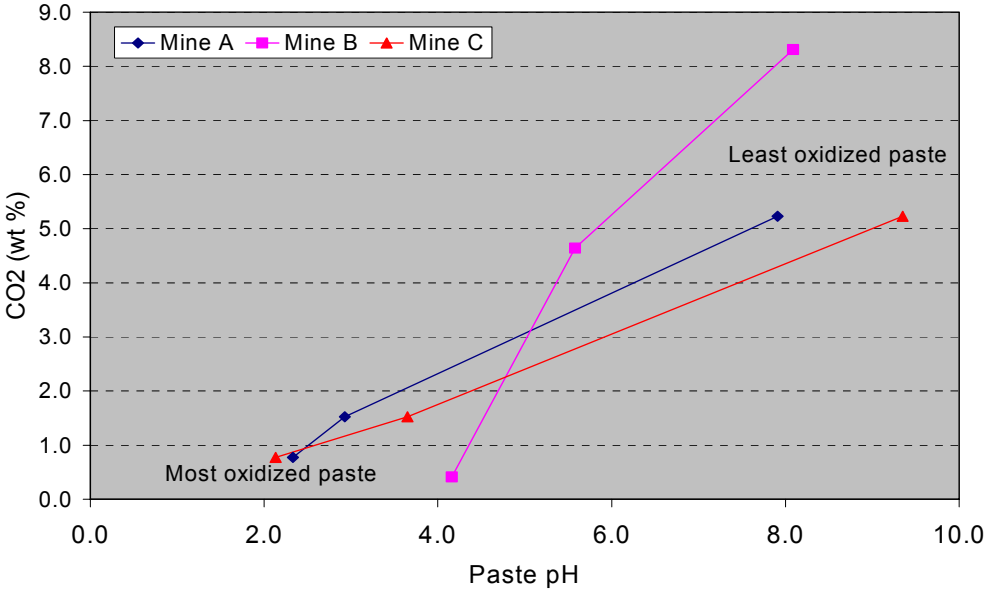

Figure 2 CO2 vs pH diagram showing the chemical transformations in the paste specimens as the high temperature oxidation proceeds.

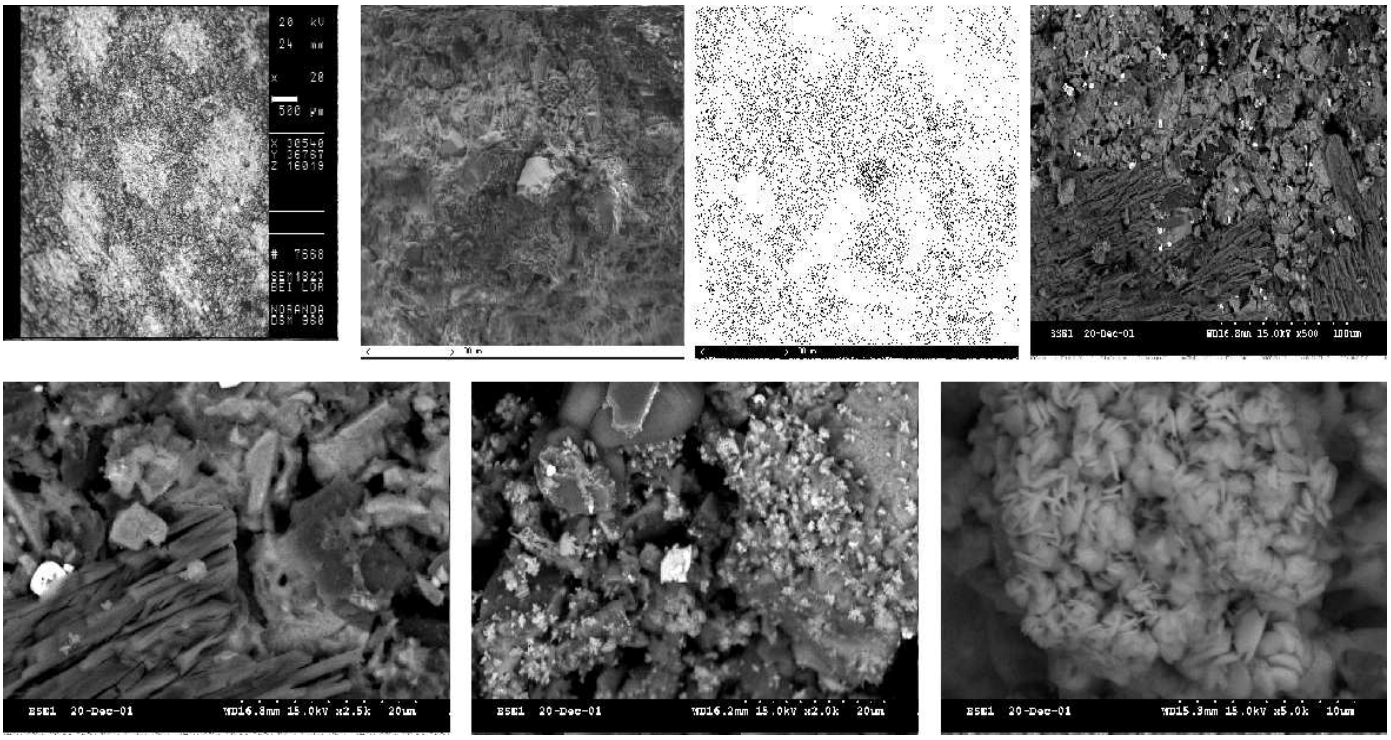

Figure 3 A) SEM photo showing secondary anhydrite-ettringite clusters in mine A red paste, 20X. B) SEM view of secondary sulfates invading the matrix in least altered paste specimen, mine B, 100X. C) EDS sulfur element mapping of area in B. The darker cluster of dots is a pyrite grain and the less dense areas are secondary gypsum. D) SEM View of a large secondary gypsum plate growing in the matrix of orange paste, mine C, 500X. E) Idem D but at a larger magnification of 2500X. F) SEM view of anhydrite clusters growing over primary minerals in mine C red lumps, 2000X. G) Idem F but at 10000X magnification.

Table 5. Reaction Paths as a Function of Temperature at Ambient Pressure.

Temperature	**Reaction**	**Gas Emission**	**Colour**
70-100°C	$CaSO_4 \cdot 2H_2O$ (Gypsum) $\Rightarrow$ $CaSO_4 \cdot H_2O$ (Bassanite) + H_2O	H_2O vapour	Grey
100-150°C	4 FeS (Pyrrhotite) + 3 O_2 + 2 H_2O $\Rightarrow$ 4 FeOOH (goethite) + 4 S^o	No gas	↓ Green
100-150°C	$S^o + O_2 \Rightarrow SO_2$	SO_2	↓
~120°C	Ettringite $\Rightarrow$ Monosulfate + Portlandite + Water	H_2O	↓
100-200°C	$CaSO_4 \cdot H_2O$ (Bassanite) $\Rightarrow$ $CaSO_4$ (Anhydrite) + Water $CaSO_4 \cdot 2H_2O$ (Gypsum) $\Rightarrow$ $CaSO_4$ (Anhydrite) + Water	H_2O	↓ Orange
250-350°C	FeOOH (Goethite) $\Rightarrow$ Fe_2O_3 (Hematite) + Water	H_2O	↓
350-400°C	FeS_2 (Pyrite) + 3 O_2 $\Rightarrow$ $FeSO_4 + SO_2$	SO_2	Red
>400°C	FeS_2 (Pyrite) + 5.5 O_2 $\Rightarrow$ Fe_2O_3 (Hematite) + 2 SO_2	SO_2	