MINERALOGICAL FACTORS CONTROLLING METAL RELEASE FROM TAILINGS AT GECO, MANITOUWADGE, ONTARIO[1]

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Geco is a polymetallic, massive sulphide orebody mined since 1957. In order to understand how solid phases control the mobility of potentially hazardous metals in the surficial environment of mine tailings, we have examined samples of ore, mill-heads, fresh tailings, and tailings that have been exposed to weathering for two to twenty years. Samples were prepared using techniques designed to preserve delicate textures and soluble secondary phases. Electron microprobe analysis has been used to identify the composition of secondary minerals. Tailings only three years old exhibit sphalerite dissolution, releasing Zn and Cd. Some Zn is attenuated by Fe-sulphate precipitation. Chalcopyrite dissolves in tailings that have been exposed for more than twenty years, and some Cu is reprecipitated as a covellite-like mineral, probably spionkopite. Feldspar also reacts with pore waters, and secondary silica replaces mica. Other secondary phases include sulphur, jarosite, and Fe hydroxides, but gypsum, a common constituent of similar tailings at other sites, is apparently absent.

Key Words: tailings, mineralogy, Geco, petrography, electron microprobe, sulphide oxidation, secondary minerals

Introduction

Secondary minerals formed as a consequence of sulphide oxidation and the development of acidic waters in mine waste act as storage sites for potentially hazardous metals. However, because some of these minerals are relatively soluble, the metals may be released from the solid phases to pore waters in response to changes in water chemistry (Alpers et al.(1)). In order to clarify how the dissolution, oxidation and precipitation of minerals determine the release or attenuation of metals, it is necessary to identify the secondary phases, determine the pertinent weathering reactions, and analyse the composition of the secondary minerals. This can only be accomplished through detailed petrographic examination of textural relationships between reactants and products.

The challenges associated with the identification and analysis of tailings minerals include the very fine grain-size and the reactivity of the material, including the tendency of some phases to dissolve in water, of others to precipitate under laboratory or storage conditions, and of still others to volatilize under the electron beam. Pioneering work in this area has been contributed by J.L. Jambor and co-workers (see Jambor (2)).

We have examined mine tailings from Geco, a massive Cu-Zn-Pb-Ag sulphide deposit in northern Ontario which has been mined continuously since 1957, in order to identify the secondary minerals, document textural evidence of *in situ* reactions and determine, using electron microprobe analysis, the composition of these phases.

The Geco Mine

The Geco massive sulphide deposit is a copper-zinc-silver-gold orebody located near Manitouwadge, 200 miles east of Thunder Bay, Ontario. It began operating in 1957 under the name Geco, the General Engineering Company who owned the mine, and has been owned and operated as the Geco Division of Noranda Mines Limited since December, 1964. The mine is an underground operation, although there is a pit quarried for backfill, and a 'glory hole' where underground mining reached the surface. Fox Creek flows through the western portion of the mine property and empties into Lake Manitouwadge, on which the town of Manitouwadge is located. Maintaining water quality in Fox Creek is an important aspect of current and future environmental planning at Geco.

To the end of August, 1994, Geco has milled 53,200,000 tons of ore containing, on average, 1.85% copper, 3.78% zinc, 1.6 ounces per ton silver and .0004 ounces per ton gold, worth over $5 billion at 1994 prices (3). The operation has produced approximately 50 million tons of mill waste. Tailings are stored in a partially flooded impoundment area northwest of the mine. Mining has also produced substantial sulphide-bearing waste rock, some of which was used, during the early years of mine development, for the construction of roads, dams and building pads.

The Geco orebody is almost completely mined out, although exploration continues at the minesite and in the surrounding area (4). Since 1991, Geco has been involved in a comprehensive closure plan to satisfy the requirements of provincial guidelines, federal guidelines and Noranda's own policy. Like most massive sulphide mines, Geco's major impact on the local environment and the primary concern of the closure plan is acid mine drainage. Further, much of the mining activity at Geco occurred during the years before the deleterious effects of waste sulphide oxidation were fully understood. Thus the current remediation plans focus on the collection and treatment of waters discharging from tailings and waste rock that have, as we show below, already undergone substantial oxidation.

The Geco mine provided an excellent site for our study of the mineralogy of mine waste because:

(1) The nature of the orebody, a polymetallic massive sulphide, and of the host rocks, silicate-rich schists and gneisses with little or no carbonate, indicates a high potential for sulphide dissolution and secondary mineral precipitation;

(2) The relatively coarse grain-size of the ore, and consequent coarse degree of crushing, has resulted in tailings fragments that are amenable to petrographic examination;

(3) The Geco mill has processed only Geco ore and the tailings are relatively homogeneous;

(4) The tailings are, for the most part, in place as deposited. In some areas the date and duration of spilling are known precisely; and,

(5) As an operating mine, Geco has generously provided records of metal production, tailings deposition, discharge water chemistry and samples of both ore and waste, as well as providing access for further sampling.

Mineralogy of the Geco Ore

Twenty-two samples of Geco ore, representing the various types present in the mine were mounted as polished sections and polished thin sections. Approximately half were collected in July 1993, some of these from underground sampling, and some from donations by the Geco staff. Other samples were taken from the teaching collection at the Department of Geological Sciences, Queen's University.

The Geco ore comprises pyrite, pyrrhotite, sphalerite and chalcopyrite, with minor galena and marcasite. Moving eastward and upward in the deposit, the ore changes from tightly-packed, coarse-grained pyrite with interstitial sphalerite and chalcopyrite, to a more Zn-rich assemblage of coarse-grained sphalerite with scattered euhedral pyrite grains (Pye, 1958).

We studied the ore mineralogy in order to define the sulphide textures and relationships present in the ore before mining, and thereby to clarify the effects of mining, milling and post-deposition weathering in the tailings sulphides.

The average grain-size in the ore samples examined is 100 microns. Pyrite is coarse-grained, sub- to euhedral and highly fractured (Figure 1). The fractures are filled with chalcopyrite, sphalerite and silicates. Pyrrhotite, predominantly hexagonal, either surrounds pyrite grains, is included in sphalerite or is intergrown with chalcopyrite and sphalerite. A late-hypogene alteration of pyrrhotite resulted in the emplacement of fine-grained pyrite and marcasite along the {0001} crystallographic planes (Figure 2). This texture appears to control the distribution of some of the secondary phases precipitated in the tailings. Chalcopyrite occurs either as rods and blebs within sphalerite grains ("chalcopyrite disease") or as larger, anhedral masses associated with sphalerite and pyrrhotite. Sphalerite is present as dendritic inclusions in chalcopyrite ("sphalerite stars") or as large anhedral grains with many inclusions of other sulphides and gangue. Galena and magnetite are associated with chalcopyrite and sphalerite as minor constituents of the ore.

Milling Procedure

In order to delimit, unambiguously, the mineral reactions that have occurred in the tailings impoundment, we need to understand what chemical changes, if any, the ore and gangue minerals undergo as a result of mining and milling processes. Thus we examined not only ore, but mill-heads and fresh tailings material - the input and output of the Geco mill.

A series of underground and surface crushers reduce the Geco ore to 65% minus 200 mesh (equivalent to 75 microns). Differential flotation is used to recover the chalcopyrite and sphalerite. Lime is added to raise the pH, nominally, to 9. Other reagents are added to suppress unwanted materials, and to froth, activate and float targeted minerals. Sodium and potassium xanthates are added during milling. As discussed in a later section, milling processes are inferred to have initiated dissolution and oxidation of pyrrhotite, and to have promoted the growth of jarosite as a secondary phase.

The mill tailings are cycloned. The coarse fraction is normally used as backfill and the finer fraction sent, as a slurry with mill waters, to the tailings impoundment (4).
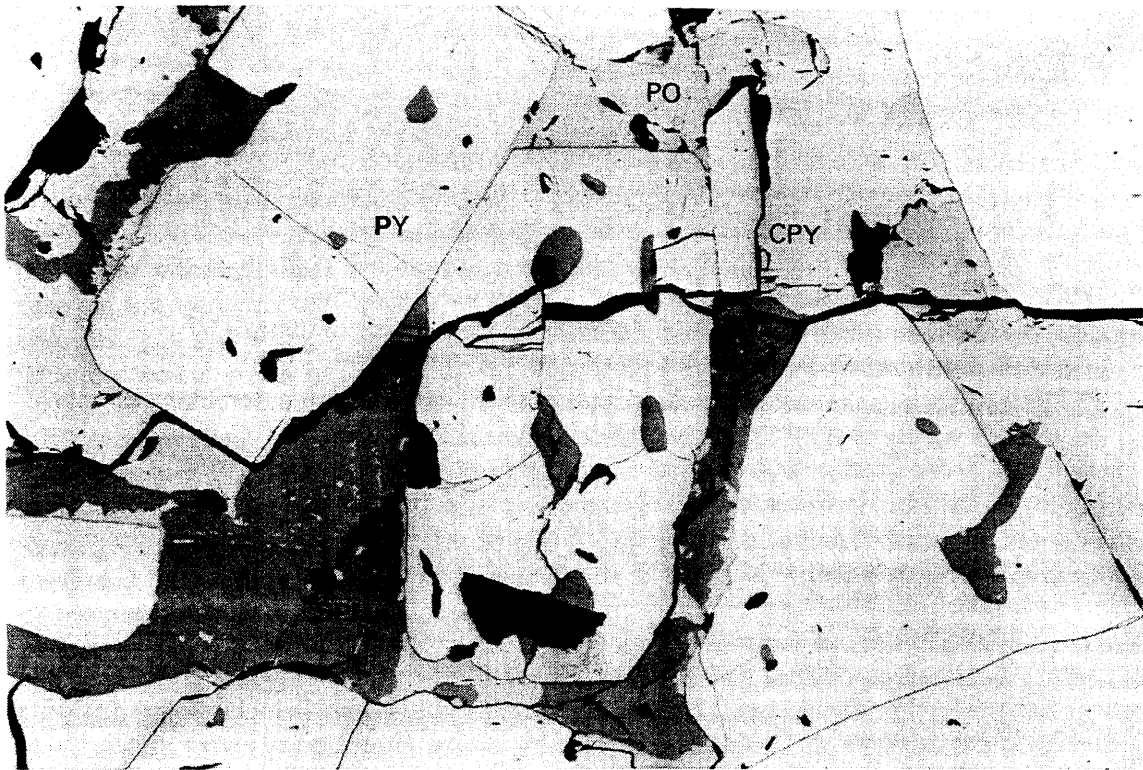
Figure 1. Subhedral pyrite (PY), typical of the Geco ore, with interstitial
sphalerite (SPH), chalcopyrite (CPY) and pyrrhotite (PO).
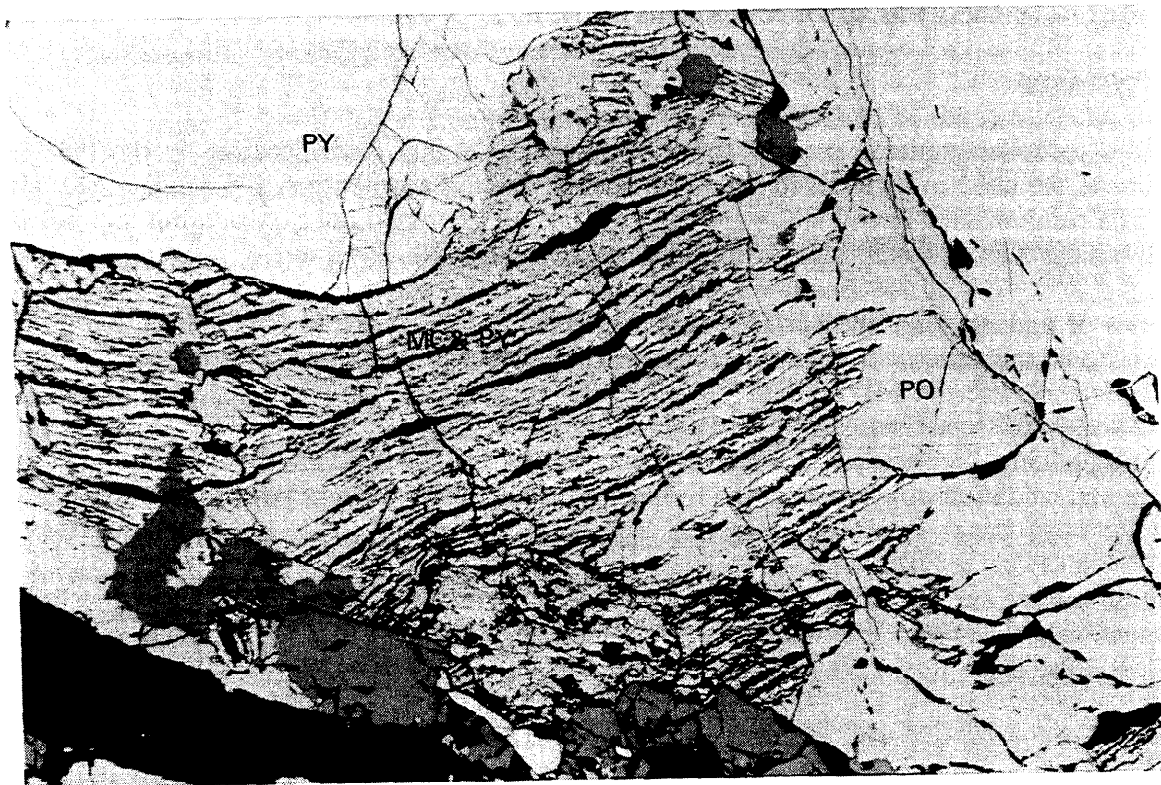Width of photograph corresponds to 40 mm. Plane-polarized reflected light.

Figure 2. Ore sample illustrating pyrrhotite alteration to fine-grained marcasite (MC)
and pyrite. Width of photograph corresponds to 40 mm. Plane-polarized reflected light.

The Geco Tailings

Sampling and Field Observations

Most of the samples examined in this study were collected at the minesite by the authors in 1993, but samples of mill-head material and fresh tails were provided by Geco staff.

One of our objectives was to examine tailings of known age and encompassing the 35-year life of the mining operation. In order to identify the textural relations between primary sulphides and gangue minerals and the secondary minerals formed as a result of chemical interaction between the tailings, the pore waters and the atmosphere, we designed a sampling technique that minimized the disturbance of grain-to-grain contacts. Although originally deposited with mill waters, most of the tailings were, at the time of sampling, above the water table and of a dry, sandy consistency. Exceptions include those from a trench dug adjacent to the standing water in the impoundment.

To identify the mineralogical changes in the tailings material over time, trenches were dug at several sites where the depositional history was known. In particular, we sampled one site where the tailings were all deposited within one month in 1991 and another site where deposition occurred over a few months in 1990. The third trench site was the Glory Hole, an area where coarse tailings (>75 microns) had been deposited between 1971 and 1973. Yet another site was chosen because it was adjacent to the surface water flooding the tailings at the time of sampling (mid-summer), thus representing conditions of intermittent subaerial exposure.

Trenches varying in depth from 50 to 75 cm were dug at the four near-surface sites in order to reveal the tailings stratigraphy. Samples were taken by driving 3" diameter PVC tubes, 1' in length, horizontally into the wall of the trench. These were then extracted, capped, and frozen during transport to Queen's. While frozen, they were cut open lengthwise with a band saw, and left to thaw and dry at room temperature.

The trenches exposed distinctive layering in the tailings, 0.5 cm to 30 cm thick, defined by abrupt colour changes from dark-grey to bright-orange or mustard yellow (Shaw, 1993). These layers do not, however, correspond simply to unoxidized and oxidized material, respectively. Petrographic inspection indicates that the orange/yellow layers differ from the grey only in that they have a slightly higher iron hydroxide content. The degree of sulphide alteration is not noticeably different. Nor can these grey and orange layers be easily attributed to particular depositional events or exposure periods. For example, samples from the site which was filled within one month in 1991 exhibit many more colour-distinctive layers than one would expect if each layer were to represent a single spill. A dark-brown "hard-pan" layer with a thickness of 5 to 8 centimetres was observed at a depth of 29 cm in the Glory Hole location.

Tailings deposited between 1957 and 1989 had been terraced into an embankment such that each terrace represents approximately one and one-half years of deposition. A sample of unconsolidated, sandy tailings was collected from each terrace in a glass jar. This material had patchy variations in colour from dark grey/green to orange/yellow. Although we were not able to sample it in such a way that *in situ* textures were maintained, it provided an opportunity to examine material that had been exposed in a particular setting for between 4 and 35 years.

Sample Preparation for Petrography and Microanalysis

Because one of the primary objectives of this study was to examine and analyse secondary minerals forming in the tailings environment, conventional methods of preparing polished thin sections could not be used. In particular, exposure to water may cause dissolution of these phases and exposure to heat may alter the minerals or accelerate reactions. Small portions of the samples were impregnated with epoxy under a vacuum such that the sandy tailings were sufficiently consolidated to be cut with a saw (without water), but the textures remained undisturbed. The thin sections were ground using kerosene and polished with an oil-based diamond paste. Initially, the kerosene was absorbed by some of the materials in the sample and interfered with electron probe microanalysis by degassing in the evacuated sample chamber. However, sections prepared with an alternate epoxy, and then polished with kerosene, proved more successful because secondary phases were preserved and the material was stable under the electron beam.

Tailings Mineralogy

Examination of the mill-head sample in thin section reveals approximately 25% opaque minerals, including 8% pyrite, 4% pyrrhotite, 6% sphalerite, 5% chalcopyrite and 2% magnetite. The pyrite is broken into sharp fragments but shows little internal fracturing, whereas the pyrrhotite, sphalerite and chalcopyrite are severely crushed and fractured, a pattern consistent with their relative hardnesses. No chemical alterations were observed to be associated with extraction.

The fresh mill tails examined consist of approximately 18% sulphides including 7% pyrite, 5% pyrrhotite, 2% sphalerite and 2% chalcopyrite (as inclusions in sphalerite and silicate minerals), in addition to 2% magnetite and trace amounts of galena and jarosite. The silicate minerals are dominantly quartz, potassium feldspar, plagioclase, muscovite and amphibole. The pyrite is broken and fragmented but displays no evidence of alteration or dissolution as a result of milling processes. The pyrrhotite exhibits slight dissolution along grain boundaries and is consistently less pink, in reflected light, than that seen in the ore. The pyrrhotite grains are also severely plucked and fractured. Neither sphalerite nor magnetite exhibits any textural evidence of dissolution as a result of milling. The only chalcopyrite grains observed were armoured by sphalerite or silicate material.

The occurrence of jarosite in the fresh tails is noteworthy. Jarosite ($KFe_3(SO_4)_2(OH)_6$) is a common secondary mineral formed in oxidized tailings (Jambor, 1994). At Geco, the milling process and the nature of the ore and gangue appear to promote the formation of jarosite in unweathered tails. The potassium may be from milling reagents or from the mica or potassium feldspar, and the iron and sulphate may originate from milling reagents or through incipient dissolution of pyrrhotite, described above.

Sulphide Dissolution in Tailings 2 to 20 years old

In tailings with deposition ages of 20 years or younger, pyrite shows no marked signs of alteration (Figure 3). Some grain boundaries appear less sharp than in fresh tails and there are agglomerations of broken pyrite and sphalerite cemented by iron hydroxide. However, in the oldest tailings, sampled from the base of the terraced embankment, pyrite is significantly reduced and exhibits obvious dissolution textures. No product solid phase of this reaction is seen.

Pyrrhotite is clearly the most reactive sulphide in the Geco tailings. Even in the fresh tails, it appears to be dissolving. In the younger tailings samples, many pyrrhotite grains have been partially replaced by minerals formed *in situ* in the tailings. In some places there is a pseudomorphic replacement of the pyrrhotite, reminiscent of the pattern of marcasite or pyrite replacement along {0001} planes, and possibly related to that pre-mining alteration (Figure 4). Elsewhere the reaction

Figure 3. Geco tailings. The pyrrhotite grain at the centre of the photo is almost completely dissolved and rimmed by Fe hydroxide. Pyrite remains unaltered. Width of photo corresponds to 40 mm. Plane-polarized reflected light.

Figure 4. Geco tailings. Pyrrhotite partially replaced by an Fe sulphate. Width of photo corresponds to 10 mm. Plane-polarized reflected light.

411

products are found as rims around the pyrrhotite grains (Figure 3). These secondary phases have been shown, on the basis of optical characteristics and electron microprobe analysis, to include Fe hydroxides, native sulphur and an oxyhydroxysulfate, possibly schwertmannite. Given this evidence for relatively rapid weathering, it is not surprising that the older tailings contain no pyrrhotite except for a few grains included in silicates and other sulphides, and thus armoured from reactive water and atmosphere.

Sphalerite is also highly reactive in the Geco tailings. Even in those deposited only two years before sampling, sphalerite is dissolving. Very irregular, strongly dissolved grains were particularly evident in the upper layers (within 20 cm of the surface) whereas samples from layers only slightly deeper (> 40 cm) consistently contained less altered sphalerite.

Chalcopyrite is present in all the younger tailings samples, although in many places the grains are enclosed within other sulphides or silicates and it is difficult to judge the response of this mineral to the oxidizing environment. However, in the older tailings from the embankment site, chalcopyrite is either noticeably absent or exhibits the effects of dissolution.

Galena is rarely seen in the Geco tailings except as apparently unaltered grains associated with magnetite. Magnetite consistently comprises 1 to 5% of the tailings and, even in the oldest material, exhibits sharp grain boundaries and no evidence of alteration.

Secondary Phases Precipitated in Geco Tailings

Secondary phases were usually identified on the basis of their optical characteristics. Electron microprobe analysis was occasionally used to confirm their identity. In some cases, textural relations such as rims or replacement indicate, unambiguously, that certain phases are the alteration products of sulphide weathering. In other cases, the secondary origin of the phases is less certain but implied by the observation that, elsewhere in the sample, the phase is present as a rim on sulphide grains.

Gypsum is notable by its absence in the samples of Geco tailings that we have studied. Jambor (2) has indicated that gypsum and goethite occur universally as secondary phases in sulphide-rich tailings, but while an iron hydroxide is common at Geco the former is not.

As described above, jarosite has been identified in fresh tails at Geco. It is also found in weathered tailings, usually as relatively large grains, not in close contact with sulphides, and rich in inclusions, particularly alkali feldspars, suggesting that these silicates are the source of potassium.

An iron hydroxide, probably goethite, is found as discrete grains and as rims on pyrrhotite (Figure 3). This is the most pervasive secondary mineral. In addition, schwertmannite ($Fe_8O_8(OH)_6SO_4$ to $Fe_8O_8(OH)_{4.8}(SO_4)_{1.6}$) has been identified in several locations in the Geco tailings on the basis of electron microprobe analysis. This is a newly-described mineral commonly found associated with ochreous precipitates from acid sulphate waters draining coal mines (Bigham, 1994, (6)). At Geco, this phase replaces pyrrhotite (Figure 4).

Native sulphur is found as discrete grains and as rims on altered pyrrhotite. It is unclear whether the isolated grains are the result of sulphide oxidation or of milling procedures.

A secondary copper mineral is observed as isolated grains and, in a few cases, as rims on chalcopyrite. This is a covellite-like mineral that assumes no purple colouration in oil immersion and may be spionkopite ($Cu_{1.32\pm0.04}S$: Goble, 1980, (7))

Silica replaces mica grains in the oldest tailings sampled from the terraced embankment, intergrown with iron hydroxide.

Secondary Mineral Chemistry and Implications for Metal Attenuation

Pore waters from the Geco tailings (8) indicate a correlation between the abundances of dissolved sulphate, Fe and Zn. This is consistent with our observations that pyrrhotite and sphalerite dissolve readily. Preliminary electron microprobe analyses of secondary phases suggest that the pervasive Fe hydroxide is sink for Zn and, to a lesser degree, Cu. However, Cu is expected to follow a pattern of mobility different than Zn, because the chalcopyrite is significantly more resistant to oxidation and dissolved Cu may be reprecipitated as covellite or spionkopite.

Acknowledgments

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