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RECOVERY AND PURIFICATION OF ARSENIC OXIDE – GIANT MINE

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MINING AND MINERAL SCIENCES LABORATORIES
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EXECUTIVE SUMMARY

At the Giant Mine, Yellowknife, Northwest Territories, the ore is milled and floated to produce a gold-rich arsenopyrite (FeAsS)-pyrite (FeS_2) concentrate. Because the ore is refractory, the concentrate is roasted to drive off the arsenic as As_2O_3 and to make the gold soluble in cyanide media. The gases from the roaster are cleaned in an electrostatic precipitator, and then are cooled to condense arsenic oxide. The As_2O_3-rich dust is collected in a baghouse and is stored on-site. The As_2O_3-rich dusts produced since 1951 have been stored underground in chambers excavated in rock. Presently 265,000 tonnes of the As_2O_3-rich dust are stored underground, and the amount increases by 8-15 t/day. The Department of Indian Affairs and Northern Development (DIAND) is considering various options to reduce or eliminate the potential environmental and health impacts caused by the stored As_2O_3-rich dust. One of the options is the reprocessing of the dust to recover a purified arsenic oxide product for the global marketplace. One means to produce such a marketable product from the As_2O_3-rich dust involves leaching with hot water to dissolve As_2O_3 selectively, purification of the solution and crystallization of an As_2O_3 product from the purified aqueous solution. A second option is the re-sublimation of the As_2O_3-rich dust to yield a pure As_2O_3 fume while leaving most of the impurities in a residue for subsequent stabilization. A third option is the use of acid media to enhance the aqueous solubility of the As_2O_3. All three routes were tested by Royal Oak Mines Inc., the former owner of the property, but technical problems were encountered with all the options. Low solubilities of As_2O_3 were found in the aqueous solutions, and high Sb contents were detected in both the crystallization and re-sublimation products. Within this framework, CANMET was contracted to investigate the production of pure As_2O_3 using water leaching-crystallization and re-sublimation techniques. The initial contract was jointly supported by DIAND and Royal Oak Mines Inc., and was inaugurated in October, 1998. It soon became apparent that the original scope of work should be expanded; accordingly, the project was amended and extended in February, 1999, to include water leaching experiments up to 200°C, the use of acid leaching media at temperatures <100°C, and further

investigations on the re-sublimation option. The amendment was authorized only by DIAND as Royal Oak Mines Inc. was in receivership at that time.

Four samples of As_2O_3-rich dust from the Giant Mine were supplied by Royal Oak Mines Inc. Two of the dust samples were recent composites, and were identified as the January 98 Composite and the April 97 Composite. These samples analyzed in excess of 87% As_2O_3, and contained ~1% Sb, as well as minor amounts of Fe, Al, Ca, Mg and Si. The two remaining samples were taken from the underground storage chambers; they were identified as the 212 Chamber and 236 Chamber. The latter samples contained only ~75% As_2O_3, as well as minor amounts of Fe, Al, Ca, Mg and Si. The 212 Chamber sample had an Sb content of 2.13%, whereas the 236 Chamber sample assayed only 0.30% Sb. The gold content of the As_2O_3-rich dusts varied from 2-11 ppm Au.

Mineralogical study of the four As_2O_3-rich dust samples, using X-ray diffraction analysis, scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and quantitative electron microprobe analysis, showed the four samples to be similar. With only a few minor exceptions, the same species are present in the four samples, and in approximately the same amounts. These species are tabulated in a qualitative manner below.

The two more recent samples, the January 98 Composite and the April 97 Composite, have similarly high As_2O_3 contents, and contain relatively small amounts of impurity oxide or silicate phases. The two older samples from the underground storage caverns, the 212 Chamber and the 236 Chamber, have less As_2O_3 but relatively high silicate contents that likely reflect non-optimal operation of the roasting circuit in the past. The Sb contents of the dusts vary from 0.30 to 2.13% Sb, and this variation affects the solid solution Sb content of the As_2O_3 crystals, as well as the amount and composition of the minor $(Sb,As)_2O_3$ phase. In all cases, the dominant arsenic carrier is Sb-bearing As_2O_3, which normally occurs as tiny euhedral crystals, but sometimes is present as large irregular masses. A minor amount of the arsenic is present as an As-bearing iron oxide and as an iron arsenate phase, in which the arsenic content varies from 1.9 to 38% As. A Ca arsenate phase and Ca-Fe arsenate phase are only minor As carriers in any of the dust samples studied. Most of the Sb in the As_2O_3-rich dust samples is present in solid solution in the As_2O_3 crystals. The Sb content of the As_2O_3 varies from 0 to 47%. The more Sb-rich compositions are actually a $(Sb,As)_2O_3$ phase. A minor amount of the total Sb substitutes for As in the iron arsenate phase, and traces of Sb occur in the Ca arsenate, Ca-Fe arsenate and Fe arsenate-sulphate phases. Unlike As and Sb, the majority of the iron occurs in silicate form or as As-bearing iron oxide. Lesser amounts of the total iron are present as iron arsenate or Ca-Fe arsenate containing 5-10% Fe. The principal silicate species are chlorite (chamosite?), muscovite and quartz; however, trace quantities of Mg silicate, Fe-Ca-Al silicate-sulphate, K-Mg-Al silicate, Na-Mg-Al silicate, Ca-Na-Mg-Al silicate, K-Al silicate (feldspar), Na-Al silicate (feldspar) Na-K-Al silicate (feldspar), $CaSO_4$, $PbSO_4$, apatite and pyrite are also detected.

Species	January 98 Composite	April 97 Composite	212 Chamber	236 Chamber
As_2O_3	major	major	major	major
Fe arsenate	minor	minor	minor	minor
$(Sb,As)_2O_3$	minor	minor	minor	trace
Ca-Fe arsenate	trace	trace	minor	trace
Fe arsenate-sulphate	trace	trace	trace	very rare
Iron oxide	trace	trace	trace	trace
Ca-Fe oxide	very rare	trace	trace	very rare
Ca sulphate	very rare	very rare	trace	very rare
Chlorite	minor	minor	minor	minor
Quartz	trace	trace	trace	trace
Muscovite	minor	minor	minor	minor

The water solubility of two lots of reagent grade As_2O_3 was determined over the temperature range from 20 to 100°C. The solubility of As_2O_3 in water increases systematically with increasing temperature, and there is generally good agreement between the data realized on heating and on cooling. Solubilities of up to 83 g/L As_2O_3 were noted, and these values agree closely with the published data for pure As_2O_3. It was further shown that all of the arsenic was present as As(III) throughout the duration of the experiments, which were done in air for periods in excess of 30 days. The solubility of reagent grade Sb_2O_3 was measured under similar conditions. The Sb_2O_3 is nearly insoluble over the entire temperature range from 25 to 95°C; the solubility at 25°C is <10 mg/L, and at 95°C, it is only 55 mg/L Sb_2O_3.

The solubility of As_2O_3 over the four As_2O_3-rich dust samples was also measured as a function of temperature on both heating and cooling. In all instances, the solubility of As_2O_3 over the dust, as determined during the heating cycle, is much lower than that determined over reagent grade As_2O_3. In fact, the solubility of any of the As_2O_3-rich dusts is only about one-half of that of pure As_2O_3, despite the ~3 day equilibration periods used at each temperature. Furthermore, there is a significantly different solubility measured on heating and on cooling. The solubility increases systematically on heating, but when the temperature is reduced, the solubility of As_2O_3 remains constant until the solubility curve for reagent grade As_2O_3 is intersected. As the temperature is reduced further, the solubility then follows the curve for reagent grade As_2O_3. The solubility of Sb_2O_3 over the four As_2O_3-rich dust samples was also determined. The measured solubilities are low; the solubility is always less than 160 mg/L Sb. The solubility of Sb determined on cooling is always higher than that realized during the heating cycle. The difference could indicate some oxidation of Sb (III) to Sb (V) during the experiments or it could reflect the strong tendency for the low concentrations of dissolved Sb_2O_3 to supersaturate in aqueous media.

There appears to be a correlation between the Sb content of the dusts and their As_2O_3 solubilities; high Sb contents result in lower As_2O_3 solubilities. The mineralogical studies of the four as-received As_2O_3-rich dusts showed that the solid solution Sb contents of the dominant As_2O_3 phase range from 0 to several percent. It is tentatively postulated that only the low-Sb As_2O_3 crystals dissolve readily in water at temperatures <100°C. Support for this hypothesis is provided by the fact that the As_2O_3 solubility increases when a very large excess of As_2O_3-rich dust is added to the reactor, and by the mineralogical studies of the leach residues which indicate a concentration of Sb-rich As_2O_3 particles in the leach residue.

The initial solubility studies indicated a low As_2O_3 solubility over the four As_2O_3-rich dusts at temperatures <100°C. Accordingly, the solubility was investigated at temperatures above 100°C using a titanium autoclave. Heating the As_2O_3-rich dusts to 125-200°C results in a significant increase in the solubility of As_2O_3, and this fact is the basis of a hot water leaching procedure proposed as one means of producing a marketable As_2O_3 product from the As_2O_3-rich dusts.

The procedure consists of leaching the As_2O_3-rich dust in water for 2h at 150°C in an autoclave to dissolve a significant amount of the arsenic. The slurry is cooled to 95-100°C, and is filtered hot, but at atmospheric pressure. The clear As_2O_3-saturated liquor is cooled to room temperature to produce a significant yield of "pure" As_2O_3 crystals. Arsenic extractions of >95% seem possible. Under the preferred conditions, the As_2O_3 crystal product contains <0.1% Sb and <0.005% Fe. Mineralogical study of the hot water leach residues confirmed the dissolution of the low-Sb As_2O_3 crystals, but showed that the Sb-rich $(Sb,As)_2O_3$ phase remained in the leach residue. As anticipated, the leach residue also collects the various silicate and iron oxide species present in the original As_2O_3-rich dusts. Also, gold concentrates quantitatively in the leach residue, and its recovery is warranted.

During the leaching of the As_2O_3-rich dusts, some Sb co-dissolution occurs, and the co-dissolved Sb can contaminate the final As_2O_3 product. Consequently, efforts were made to remove the Sb from the aqueous solution using four ion exchange resins (Gravex GR-2-0, Amberlite IRC 120, Amberlite IRC 50 and Duolite C467) and activated carbon (Hycarb 6x12). Unfortunately, none of the ion exchange resins removed any significant amount of Sb from the water leach solutions at either 25°C or 95°C. The activated carbon removed ~25% of the Sb, but co-extracted major amounts of As as well. The negative results likely are a consequence of the absence of cationic antimony species in the near-neutral aqueous media. In contrast, cationic antimony species are present in acid media. Reducing the pH of the solutions to pH 3.0 had little effect on the extent of Sb extraction, but reducing the pH to 1.0 resulted in the removal of a significant amount of the dissolved Sb. In particular, the Duolite C467 resin extracted >90% of the Sb, and the extent of extraction likely could be increased by optimization of the extraction parameters. Although ion exchange holds little promise for the removal of Sb from near-neutral water leach solutions, it probably could be employed to purify the liquors generated in an acid leaching circuit.

Controlled re-sublimation of the as-received As_2O_3-rich dusts should enhance the purity of the As_2O_3 product and should completely reject the non-volatile oxide and silicate species. It was shown, in fact, that re-sublimation effectively rejects all impurities except for Sb. The Sb content of the re-sublimed

As_2O_3 product increased as the temperature increased and as the duration of the re-sublimation tests increased. Oxidizing atmospheres (air or O_2 gas) yielded higher quality As_2O_3 products than the use of neutral (N_2 or He gases) or reducing (H_2 gas) atmospheres. A direct comparison of the thermal behaviour of the four As_2O_3-rich dusts was made by heating each dust at 545°C for 10 h in static air. There is a near-linear relationship between the As/As+Sb percentage of the As_2O_3 product and the As/As+Sb percentage of the as-received As_2O_3-rich dust. As anticipated, all of the initially present gold remains in the sublimation residue. The results reflect a persistent re-sublimation of Sb, despite the significant difference in the boiling points of Sb_2O_3 and As_2O_3. Limited mass spectrographic work done in support of the study, however, detected mixed arsenic-antimony vapour species, notably As_3SbO_6, in the vapours over the As_2O_3-rich dust. Such mixed As-Sb oxide species have a vapour pressure greater than that of end-member Sb_2O_3, and presumably account for the vapour transport of Sb, even at relatively low temperatures. Efforts to control the transport of Sb by the addition of metallic arsenic to the system were not especially successful. Supporting mineralogical studies of the re-sublimation residues detected major amounts of iron arsenate ($Fe_2As_4O_{12}$ or $FeAs_2O_3$ having a minor Sb content), $CaSO_4$, muscovite, chlorite and quartz. Less abundant species include Ca arsenate, Na-Al silicate, As-bearing iron oxide, a rare Fe-Zn arsenate phase, and possibly, elemental arsenic. Large masses of As_2O_3 were sometimes present, but these particles may have spalled from the walls of the reaction tube during sample collection. Overall, the re-sublimation studies indicate a persistent transport of Sb that may be difficult to control if rapid re-sublimation rates and high As_2O_3 product recoveries are sought.

A series of scoping tests was done to evaluate the possibility of enhancing the solubility of As_2O_3 over the as-received As_2O_3-rich dusts by using acid media in place of water. The presence of nitric acid, hydrochloric acid or sulphuric acid results in the rapid dissolution of As_2O_3 from the As_2O_3-rich dust, such that near-steady state solubilities are realized in less than 30 min. Furthermore, the extent of As_2O_3 solubility is greatly enhanced, relative to that in water. As expected, the solubility of As_2O_3 in acid media increases with increasing temperature, and with increasing initial pulp density to the point where solution saturation is achieved. Although the solubility of As_2O_3 increases slightly with increasing HCl concentration, it decreases with increasing HNO_3 concentration, for concentrations at least as high as 4.0 M HNO_3. The three acids yielded similar As_2O_3 solubilities, and their efficacy may be related to their ability to solubilize Sb. That is, it is believed that the acid solubilizes at least part of the Sb, thereby minimizing its "passivation" effect on the dissolution of As_2O_3. A negative consequence of this behaviour is the presence of relatively high Sb (and Fe) concentrations in the acid leach liquor. Fortunately, ion exchange resins can remove Sb from acidic media, and a number of techniques exist to control the dissolved Fe. Cooling of the hot acid leach liquors to 25°C resulted in the precipitation of large amounts of As_2O_3. Efforts to increase the yield of As_2O_3 crystals by neutralizing the solution after As_2O_3 crystallization were not successful. Only very small amounts of an amorphous or poorly crystalline phase were formed when the solutions were neutralized to pH 9.0 with Na_2CO_3.

Overall, this study has shown that "pure" As_2O_3 can be produced from the As_2O_3-rich dusts generated at the Giant Mine by using hot water leaching, acid leaching or re-sublimation techniques. The traditional problems associated with water leaching seem to have been overcome by the use of an autoclave to increase the leaching temperature to ~150°C. Of the three options considered, the hot water leach procedure seems to control impurities most effectively. Acid leaching, however, offers advantages over water leaching with respect to the rates of dissolution, the As_2O_3 solubilities and possibly the costs, because of the avoidance of autoclave processing. It suffers in that the Sb and Fe impurities in the As_2O_3-rich dusts are more extensively solubilized. Also, the effectiveness of this technique for more Sb-rich dusts requires demonstration. Re-sublimation of the As_2O_3-rich dusts effectively controls the oxide and silicate impurity species, but is much less effective in eliminating Sb. The present results suggest that it would not be possible to control Sb adequately during the re-sublimation of Sb-rich dust feeds. Of course, the production of any marketable As_2O_3 product implies a growing market for the oxide. Consequently, the further development of any of these options should await an extensive evaluation of the market potential of As_2O_3, although the hot water leach procedure could be a component of an overall arsenic stabilization program for the As_2O_3-rich dusts from the Giant Mine.

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INTRODUCTION

The Giant Mine, Yellowknife, Northwest Territories has been in operation for over fifty years and has produced 6,800,000 oz of gold in that period. Ore reserves, however, are nearly exhausted. In fact, at the present price of gold, calculated ore reserves are adequate for less than two years of operation. Until very recently, the mine was operated by Royal Oak Mines Inc., but that company was declared bankrupt in 1999.

At the Giant Mine, the ore is crushed, milled and then is floated to produce an arsenopyrite ($FeAsS$)-pyrite (FeS_2) concentrate. The concentrate is refractory, and accordingly, is subjected to roasting in a series of two slurry-feed Dorr-Oliver roasters to drive off the sulphur as SO_2 and the arsenic as As_2O_3. A two-stage roasting operation is required to ensure the total evolution of the arsenic as As_2O_3 and the compete liberation of the gold for subsequent cyanidation. Gases from the roaster train are passed through a hot electrostatic precipitator to collect any carried-over calcine, which is recycled to the gold extraction circuit. The gases are then cooled, by admitting dilution air, to condense the arsenic oxide. Finally, the As_2O_3 fume is collected in a baghouse, which operates with a solids collection efficiency of 99.9%. The collected As_2O_3-rich dust is easily fluidized and is subsequently transported pneumatically (1).

The As_2O_3-rich dusts produced since 1951 have been stored underground, in chambers excavated in coherent bedrock. Presently, 265,000 tonnes of the As_2O_3-rich dust are stored underground in 15 chambers, and 8-15 t/day of new dust is accumulating. It is reported that, on average, the accumulated dust contains 76% As_2O_3 and 0.54 oz/t Au; however, localized gold concentrations as high as 2 oz/t Au have been analyzed. The dust presently produced is reported to contain 89% As_2O_3 (67.7% As), 1.04% Sb, 1.68% Fe and 0.14 oz/t Au. Recent mining activities have disturbed the permafrost seal in some of the chambers, and some arsenic contamination of the mine waters is occurring. Accordingly, the As-containing mine waters are pumped to the surface, where they are oxidized with hydrogen peroxide (H_2O_2) and then are treated with lime (CaO) and ferric sulphate ($Fe_2(SO_4)_3$) to precipitate an insoluble amorphous iron arsenate compound for storage in a residue pond (1).

The Department of Indian Affairs and Northern Development (DIAND) has the responsibility as regulator to ensure that the environment of the Northwest Territories is protected and that human health is maintained. Accordingly, DIAND is considering various options to reduce or eliminate the potential environmental and health impacts caused by the stored As_2O_3-rich dusts. One of these options is the reprocessing of the dust to recover a purified arsenic oxide product which could be used in the wood preservative industry or for other applications. Although the value of As_2O_3 is only U.S. $0.20-$0.30/lb, the manufacture of any product would remove the arsenic from the mine site and convert it into a useful commodity. For such applications, it is claimed that the product must contain >98% As_2O_3, but less than 0.2% Sb and 0.02% Fe, although the need for such low Sb and Fe specifications for wood preservative applications is not clear.

One means to produce a marketable arsenic product from the As_2O_3-rich dusts involves leaching with hot water to dissolve As_2O_3 selectively, filtration to reject insoluble matter, removal of any co-solubilized Sb from solution to meet product specifications, and crystallization of a pure As_2O_3 product from the aqueous medium. Preliminary testwork on the water leaching option was carried out by Royal Oak Mines (private communication of L. Connell, Royal Oak Mines Inc., 1998). Using a residence time of 30-240 minutes at 95°C, the company was able to achieve >90% As dissolution, while rejecting ~80% of the Sb to the residue. Negligible iron dissolution occurred. Over 80% of the mass of the initial dust dissolved; the residue amounted to about 17% of the initial mass and contained 39% As. The solution generated at 95°C analyzed 31 g/L As, 92 mg/L Sb and 6 mg/L Fe. The observed As solubility of 31 g/L As, however, is much less than the reported solubility of ~100 g/L As_2O_3 (~75 g/L As) (2). The reasons for the low solubilities over the As_2O_3-rich dusts are not known, but they could be partly attributable to the relatively short leaching times used (<4 h) or to the low pulp densities employed (~5% solids). Because of the low arsenic solubilities realized, the yield of As_2O_3 crystals during the subsequent cooling of the solution to ambient temperature was unacceptably low. In the Royal Oak work, this problem was addressed by evaporation of the ~95°C solution to about one-third of its initial volume prior to cooling to room temperature to crystallize As_2O_3. Efforts were also made to remove part of the co-dissolved Sb using two ion exchange resins and activated carbon. The use of the ion exchange resins or activated carbon allowed the crystallization of a product containing ~100% As_2O_3, <0.2% Sb and <0.05% Fe. Hence, it appears that the simple water leaching-crystallization technique can yield an As_2O_3 product which satisfies the purity requirements of the marketplace. The major difficulty with this processing option seems to be the low As_2O_3 solubilities produced in the leaching part of the process that result in a commercially unacceptable yield of As_2O_3 crystals unless costly techniques, such as solution evaporation, are employed.

A second option to produce a pure As_2O_3 product is the controlled re-sublimation of the As_2O_3-rich dust to collect a pure As_2O_3 fume while leaving most of the impurities in a residue for subsequent treatment and stabilization. This option was pursued by Royal Oak Mines using the Warox process (1). Their test work showed that it was possible to re-sublime the As_2O_3-rich dust to yield a fume containing 99.3-99.8% As_2O_3, together with less than 0.05% Fe. Significantly, the Sb contents of the sublimates ranged from 0.13 to 0.59% Sb. Careful study of the low-Sb products, however, indicated that they tended to originate from low-Sb dusts. That is, there was little selective re-sublimation of As_2O_3 relative to Sb_2O_3. Although re-sublimation can control most of the impurities in the dust, the behaviour of antimony remains a concern with this option.

Within the above framework, CANMET was contracted to investigate the production of pure As_2O_3 using water leaching-crystallization and re-sublimation techniques. The initial contract was jointly funded by DIAND and Royal Oak Mines Inc. and was initiated in October, 1998. During that study, it became apparent that the originally proposed scope of work needed to be expanded, and as a consequence, the original project was amended and extended in February, 1999. The amendment was authorized only by DIAND as Royal Oak Mines Inc. was in receivership at that time.

The scope of the original and amended project involves the production of pure As_2O_3 by water leaching-crystallization and by re-sublimation of four As_2O_3-rich dust samples provided by the company. The water leaching work was intended to measure the solubility of As_2O_3 in water as a function of temperature on both heating and cooling. Because low solubilities were initially measured, they were subsequently determined at temperatures up to 200°C with the use of a high pressure autoclave. These latter tests suggested a possible processing procedure that involves autoclave leaching, cooling of the slurry to 95-100°C, followed by filtration and the subsequent cooling of the solution to room temperature to crystallize pure As_2O_3. Efforts were also made to leach the As_2O_3-rich dusts in acid media. Sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) were evaluated for this application, and subsequently, a number of leaching parameters was examined using hydrochloric acid or nitric acid as the leaching media. Moderate As_2O_3 solubilities were realized in the acid media, and acid leaching seems to offer some advantages over water leaching. Attempts were made to remove the low concentrations of co-dissolved Sb from the water and acid leach liquors using four ion exchange resins and activated carbon. These studies were done at various temperatures to try to optimize the level of antimony removal. Re-sublimation tests were carried out for different times at various temperatures and gas flow rates to try to enhance the vaporization of As_2O_3 relative to Sb_2O_3. The use of oxidizing, neutral and reducing atmospheres was explored. The initial results on the re-sublimation of As_2O_3 from the dusts indicated that the greatest selectivity of As_2O_3 over Sb_2O_3 occurred at the lowest temperatures, where unfortunately, mass transport of the vapour is also low. Consequently, the use of controlled re-sublimation at low temperatures was investigated to try to obtain a high level of As_2O_3 selectivity over Sb_2O_3, together with an acceptable re-sublimation rate. To complement the re-sublimation activities, a preliminary mass spectrographic study of the vapour produced from one of the dusts was done to ascertain whether mixed $(As_{4-x}Sb_x)O_6$ molecules were present, or whether the vapour consisted only of As_4O_6 and Sb_4O_6 entities (3). In support of both the water leaching and re-sublimation activities, detailed mineralogical studies were carried out on the as-received As_2O_3-rich dust samples and on some of the intermediate products. The mineralogical activities focussed on the As-, Sb- and Fe-containing phases rather than on the gold content of the dusts. This report summarizes the results of the above exploratory investigations, and also offers some observations on their implications for the recovery of a marketable As_2O_3 product from the As_2O_3-rich dusts stored at the Giant Mine.

EXPERIMENTAL

Samples

Four samples of As_2O_3-rich dust from the Giant Mine were supplied by Royal Oak Mines Inc. Two of the dust samples were recent composites, and were identified as the January 98 Composite and the April 97 Composite. The remaining two samples were taken from the underground storage chambers, and were identified as 212 Chamber and 236 Chamber. All four samples were fine powders; three of the dusts were dry, but the 236 Chamber sample was slightly damp. All four samples, however, were used without further treatment. Reagent grade arsenious oxide (J.T. Baker, 99.95% As_2O_3) and reagent grade antimony trioxide (J.T. Baker, 101.4% Sb_2O_3) were sometimes used for comparative experimentation; the reagent grade oxides also were used in the as-received state.

Mineralogical Techniques

X-ray powder diffraction analyses were carried out on the four as-supplied samples, on the reagent grade As_2O_3, on some of the water leach and acid leach residues, and on some of the re-sublimation products using a Rigaku automated diffractometer with a water-cooled rotating copper anode. The detection limit of most crystalline compounds by this apparatus is 1-3%, depending on the number of phases present and their diffracting powers. Polished sections of the samples were prepared, and these were then examined using scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX). Extensive use was made of the backscattered electron detector at high magnification to distinguish compositionally different phases. Some of the phases were analyzed quantitatively with a JEOL-8900 electron microprobe operated at 20 kV and a 20 nanoampere beam current. In some instances, loose powder mounts of the samples, wherein the material was sprinkled loosely on the stage of the electron microscope, were examined with the SEM to show the morphology of the particles more fully. Details of the various mineralogical procedures have been reported previously (4).

Solubility Measurements

The solubility experiments were done in a 2-L reaction vessel having a tight-fitting ground glass lid to prevent water evaporation during the course of the experiments. As shown in Figure 1, a thermometer (±0.1°C), a water-cooled condenser which was loosely stoppered, and a sampling tube closed at the bottom with a medium porosity glass frit were fitted in the lid of the vessel. The sampling tube with the fritted glass disk extended into the middle of the test slurry. The reaction vessel and its contents were heated in a temperature-controlled circulating oil bath regulated to better than ±0.1°C. The actual temperature of the solution was measured by the thermometer suspended in the slurry. The reaction vessel containing ~1.5 L of solution with an excess of dust (~150 g) rested on the bottom of the oil bath, and the slurry was stirred magnetically from beneath.

The solubility measurements were performed as follows. One and a half litres of water were placed in the 2-L reaction vessel together with an excess of the As_2O_3-rich dust or reagent grade As_2O_3 and Sb_2O_3. The contents were then stirred for ~3 days to attain equilibrium. Preliminary experiments showed that the dusts equilibrated slowly in water; three days were required to reach saturation at room temperature and one day was required at 60°C. Significantly, most of the solubility measurements carried out previously by Royal Oak Mines used equilibration times of <4 h. When equilibrium had been attained, a clean fritted sampling tube was immersed in the liquid and was thermally equilibrated. Saturated solution was then drawn through the frit into the sampling tube by the application of suction at the open end. When the sampling tube within the reaction vessel was partly filled with the filtered solution, the suction attachment, which fitted into the open end of the sampling tube in the lid of the vessel, was removed and samples of the hot solution were taken using 5 mL glass pipettes. The pipettes were previously calibrated as a function of temperature using pure water and the same sampling procedure as that employed for the As_2O_3-saturated solutions. A solution sample was taken at each temperature. The sample was diluted directly into 100 mL or 500 mL of 2% HNO_3 contained in a volumetric flask; the dilution factor was sufficiently large that crystallization of As_2O_3 or Sb_2O_3 never occurred. The contents of the volumetric flask were brought to volume, and the solution was analyzed for As by ICP analysis and for Sb and Fe by ICP-mass spectroscopy. In some instances, a second sample was taken at the various temperatures. These samples were discharged directly into a weighing bottle, sealed, cooled to room temperature, and weighed; this sample allowed the density of the saturated solution to be calculated, if required.

After the samples were taken, the solution temperature was increased to 100°C in 10°C increments, with samples being taken at each incremental temperature. The solution was then cooled to ~95°C, and subsequently, in 10°C increments to room temperature or to 5°C to obtain saturation curves on both heating and cooling. Agreement between the data obtained on heating and cooling is necessary if "equilibrium" solubilities are to be reported.

The solubilities were calculated from the measured concentrations, the dilution factor and the volume of the calibrated pipette. In this report, the arsenic solubilities are reported as g/L As_2O_3, whereas the antimony and iron solubilities are reported as g/L Sb and g/L Fe. It should be stressed that the reporting formulae are purely formal and do not indicate the species actually present in solution.

Autoclave Solubility-Leaching Tests

These experiments were carried out in a Parr 2-L titanium autoclave fitted with a glass liner and titanium internals. The As_2O_3-rich dust and water were placed in the autoclave, which was sealed and then heated rapidly to the desired reaction temperature of 125-200°C. Because of the high temperatures used in the autoclave solubility experiments, solution saturation was achieved in just a few hours. In this regard, retention times were measured from the moment that the operating temperature was reached, although it is recognized that some dissolution occurs during the heat-up period. The experiments were done without an applied gas pressure; that is, the tests were effected only under the steam pressure generated by the system. At the end of the reaction period, the autoclave was rapidly cooled (~5 min) to 95-100°C by the use of the internal water cooling coil. Of course, at temperatures <100°C, the pressure in the autoclave is that of the surrounding atmosphere. The autoclave was opened at 95-100°C, and the slurry was rapidly transferred to a solubility reactor heated to 95°C in its oil bath. The solubility reactor was sealed, and then equilibrated for 2-3 days at 95°C. A sample was taken for a solubility determination and the vessel was then cooled to room temperature. The procedure for determining the solubilities is described above.

In those experiments intended to produce As_2O_3 crystals, the autoclave slurry at 95-100°C was filtered hot using a Buchner vacuum filter with Whatman No. 3 paper; the apparatus was preheated to ensure that the temperature of the filtrate was always ~95°C. Following filtration, the solution was transferred to a beaker and was allowed to cool to room temperature while being gently agitated. It was found that As_2O_3 crystals formed spontaneously and without the need for As_2O_3 seed additions. When crystallization was complete (~16 h), the product was filtered using Whatman No. 3 paper. The various precipitates were collected, dried at 110°C, weighed, and analyzed if required.

Antimony Removal by Ion Exchange or Activated Carbon

Four commercial ion exchange resins were selected on the basis of previous experiments carried out by Royal Oak Mines and on information published in the open literature. These resins were considered to be the most promising for the removal of antimony from concentrated As_2O_3-containing media under neutral or acid pH conditions. Samples of the resins were obtained from the manufacturers, and Table 1 presents a list of the four ion exchange resins evaluated. The resins were hydrated for 24 h, washed with copious amounts of water and then used without additional treatment.

Table 1 - Ion Exchange Resins Tested for Antimony Removal

Resin	Type	Manufacturer
Gravex GR-2-0	Sulphonic	Graver Technologies
Amberlite IRC 120	Sulphonic	Rohm and Haas
Amberlite IRC 50	Carboxylic	Rohm and Haas
Duolite C467	Aminophosphonic	Rohm and Haas

Equilibrium extraction experiments were carried out by contacting appropriate amounts of the individual resins with the Sb-containing As_2O_3-rich solution, while applying gentle mechanical agitation. For most experiments, the amount of resin is expressed as the "wet settled volume", as is common practice in ion exchange applications. In some experiments, however, where a direct comparison with activated carbon was desired, the actual resin weight was used instead of the resin volume. In all the experiments, the extent of antimony removal was calculated from the Sb concentration of the aqueous solution before and after its contact with the resin. Total Sb was analyzed, and no effort was made to differentiate Sb(III) from Sb(V).

In addition to the four ion exchange resins given in Table 1, an activated carbon sample, Hycarb 6X12, was also evaluated for its Sb removal potential. The activated carbon was washed with water prior to use.

Re-sublimation of the As_2O_3-Rich Dusts

The overall objective of this part of the investigation was to re-sublime the as-received As_2O_3-rich dusts to produce a pure As_2O_3 product. These experiments were carried out using a horizontal tube furnace which was 60 cm in length. A fused silica tube 90 cm long by 60 mm outside diameter was positioned in the tube furnace such that ~25 cm of the tube protruded on one side. The As_2O_3-rich dust was weighed and placed in an alumina crucible which was positioned in the constant temperature (±2°C) hot zone of the furnace. Rubber stoppers were used to seal the ends of the tube, and the stoppers were fitted with ports for the entry and exit of gases and for a temperature measuring thermocouple. Gas was sometimes passed through the tube to help transport the volatilized As_2O_3 to the cooler part of the tube where it condensed as a "ring" on the surface of the glass. At the completion of the experiment, the tube was removed from the furnace and was cooled. The condensed oxide product was removed and analyzed. The re-sublimation experiments were carried out at various temperatures and, sometimes, for different degrees of sublimation. Comparative tests were done using slowly-flowing oxygen, inert gas and hydrogen to assess the influence of the gaseous atmosphere on the relative transport of As_2O_3 and Sb_2O_3. Finally, screening experiments were done wherein the dust was heated with As metal to try to remove any vapourized antimony oxide from the gas stream prior to the condensation of the As_2O_3. To complement the vapourization studies and to provide a fundamental rationale for the co-sublimation of antimony at temperatures significantly below the 1550°C boiling point of Sb_2O_3, a preliminary mass spectrographic study of the vapours was carried out. This work was sub-contracted to the Université de Montréal and was based on the use of a Micromass Autospec-OA time-of-flight mass spectrometer operating in the EI mode at 70 eV. The samples were heated to 300°C on a solid probe to vapourize the arsenic and antimony oxide species into the mass spectrometer.

Arsenic Solubility in Acid Media

The intent of these experiments was to evaluate the possibility of enhancing the solubility of As_2O_3 over the As_2O_3-rich dusts by the use of acid media in place of water. These scoping experiments were done using the 236 Chamber sample which contains 0.30% Sb. The acid leaching experiments were carried out in 2-L glass reaction kettles contained in a temperature-controlled oil bath. One litre of the acid solution was heated to 95°C, and at that point, a known mass of the As_2O_3-rich dust was added and was stirred for the duration of the experiment, generally 2 h. The acids initially evaluated were 2.0 M HCl, 2.0 M HNO_3 and 1.0 M H_2SO_4. For the experiments using the different acids, solution samples were taken at various time intervals by drawing the liquid through an in-line filter. The collected solutions were stored in a water bath at 95°C. Subsequently, they were accurately pipetted, diluted to a known volume and finally analyzed to assess the extent of arsenic dissolution as a function of time. Based on these initial tests, nitric acid (HNO_3) and hydrochloric acid (HCl) were selected for further experimentation. The parameters investigated in this latter part of the study were the acid concentration (1.0, 2.0, 3.0 and 4.0 M HNO_3; 0.75, 2.0 and 3.0 M HCl) the leaching temperature (95°C, 75°C and 55°C) and the initial solids content of the slurry (75 g/L, 125 g/L and 175 g/L solids). In fact, all the pulp densities reported are the initial values before any dissolution of As_2O_3 occurred. For the latter experiments, solution sampling as a function of time was not done. Rather, leaching was carried out for a constant 2-h period. At that time, the slurry was filtered while hot, and the filtrate was collected. The leach residue was water-washed, dried at 110°C, and analyzed by X-ray powder diffraction methods. The filtrate was then cooled to room temperature to allow As_2O_3 to crystallize. The As_2O_3 crystals were filtered, dried at ~60°C, weighed and also analyzed by X-ray diffraction methods. In some tests, the solution remaining after the filtration of the As_2O_3 crystals was neutralized to pH 9.0 with solid, reagent grade Na_2CO_3 to try to precipitate additional As_2O_3. The resulting precipitate was filtered, dried at 110°C, and then analyzed by X-ray powder diffraction techniques to identify the arsenic compounds precipitated. Neither the As_2O_3 products nor the neutralization precipitates were water washed in order to avoid the dissolution of the As_2O_3.

RESULTS AND DISCUSSION

Samples

The four samples of As_2O_3-rich dust supplied by Royal Oak Mines were analyzed at CANMET; the results are presented in Table 2. The recent composite samples have As contents in excess of 66% As (>87% As_2O_3), but also contain modest amounts of Sb, Fe, Al, Ca, Mg and Si. The two samples from the underground chambers have much lower As contents (56-58% As), but also contain minor amounts of Sb, Fe, Al, Ca, Mg and Si. The Sb content is a concern for the marketing of any As_2O_3 product, and the Sb contents of the as-received dusts are variable. They range from 0.30 to 2.13% Sb. The data of Table 2 support the view that the stockpiled dusts have higher gold values than the dusts presently being generated.

Table 2 - Chemical Compositions of the Four As_2O_3-rich Dust Samples Provided by Royal Oak Mines (wt %)

Element	January 98 Composite	April 97 Composite	212 Chamber	236 Chamber
As	68.2, 68.7	66.7, 69.6	56.2	58.0
Sb	0.87, 0.84	1.48, 1.49	2.13	0.30
Fe	1.23, 1.17	0.78. 0.81	2.62	1.66
Al	0.64, 0.64	0.33, 0.33	1.06	0.92
Ca	0.46	0.37	0.65	0.57
Mg	0.24, 0.26	0.13, 0.13	0.37	0.36
Si	1.05, 1.09	0.61, 0.61	2.07	1.81
Au(ppm)	2.2	2.4	11.0	5.1

Mineralogical Characterization of the Four Dust Samples

X-ray diffraction analyses of the two lots of reagent grade arsenic oxide indicated only As_2O_3 having the cubic arsenolite structure. Analogous X-ray diffraction analyses of the four dust samples showed them to be very similar, *inter alia*, despite the minor differences in chemical composition indicated in Table 2. The X-ray diffraction patterns of the four dust samples are presented in Appendix 1. All four samples consist of major amounts of As_2O_3 of the arsenolite structure, together with minor amounts of a chlorite-type mineral (chamosite?) having the general formula of $(Fe,Al,Mg)_6(Si,Al)_4O_{10}(OH)_8$. A trace quantity of muscovite, $KAl_2(Si_3Al)O_{10}(OH,F)_2$, is also evident. Quartz is present in trace amounts, but the detection of quartz is made difficult because the strong line of quartz overlaps that of muscovite. The amounts of chlorite, muscovite and quartz, relative to arsenolite, vary somewhat from sample to sample, but arsenolite is always the dominant phase. The four dust samples were supplied in large plastic pails. To investigate the possibility of sample segregation within the pails, X-ray diffraction analyses of material from the top and bottom of each pail were carried out. The spectra from the top and bottom of a given pail were identical, and the implication is that the supplied samples themselves are relatively homogeneous.

Characterization of the January 98 Composite Sample

Detailed SEM-EDX study of the dust provided considerably more insight into the phases present. Figure 2 presents a general view of the January 98 Composite sample. This sample consists mostly of As_2O_3 which commonly occurs as 1-3 µm free crystals or as somewhat larger crystal agglomerates. Many of the As_2O_3 crystals demonstrate an octahedral morphology characteristic of arsenolite. The large and darker appearing particles are chlorite (chamosite ?) or quartz. Tiny bright appearing grains of iron oxide having a minor As content are also present. The EDX study of the As_2O_3 particles commonly detected trace amounts of Sb; similar studies showed the chlorite to contain major amounts of Mg, Al and Si, along with traces of Fe, K and Na.

Figure 3 is a backscattered electron micrograph of the same sample as seen in polished section. The arsenolite (As_2O_3) occurs abundantly as tiny bright appearing crystals or crystal aggregates. The EDX study of the As_2O_3 commonly detected a trace-to-minor amount of Sb. The larger platy crystals are chlorite, whereas the dark appearing irregular grains are usually quartz. Of note are a number of 1-3 µm calcium arsenate particles having a minor or trace S content. Occasionally, large masses of As_2O_3 or $(As,Sb)_2O_3$ are detected, and one such mass is illustrated in Figure 4. Although the majority of the image shown in Figure 4 consists of 1-3 µm euhedral As_2O_3 crystals and somewhat larger grains of As-bearing iron oxide, a >50 µm mass of As_2O_3 having a trace Sb content is also evident. Such masses of As_2O_3 are moderately abundant in this sample, but nevertheless, constitute only a small percentage of the total As_2O_3 present. The mechanism of formation of these large masses of As_2O_3 is not known, but they may represent spalled accumulations from the roof or ducting of the baghouse.

Rarer masses of $(Sb,As)_2O_3$ are also detected, and one such occurrence is shown in Figure 5. The mass is 40-50 µm in size, and is irregular in form. Its brighter appearance reflects the elevated Sb content of this phase, which seems to be an As-bearing Sb-rich oxide; i.e., $(Sb,As)_2O_3$. The mechanism by which such Sb-rich oxide particles form in the baghouse is unknown.

An iron arsenic-oxide phase occurs in minor amounts in the January 98 Composite sample, and the iron arsenic-oxide ranges in composition from As-bearing iron oxide to compositions approaching iron arsenate. Figure 6 illustrates a ~20 µm mass of iron oxide containing minor amounts of As as well as traces of Sb. The iron oxide particle has a banded texture that may reflect the cyclical oxidation of a grain of pyrite. Variations in the grey level of the iron oxide reflect local variations in the As content. In this instance, it seems that the morphology of the original iron-bearing particle has been faithfully preserved. Figure 7 illustrates a ~100 µm porous mass of iron arsenate that is associated with a large mass of As_2O_3 and numerous tiny As_2O_3 crystals. The iron arsenate phase contains major amounts of iron and arsenic, as well as a minor-to-major S content. It is likely an iron arsenate phase having a significant sulphate ion substitution for arsenate. The morphology suggests a complex formation mechanism that likely involves the diffusion of both As and Fe.

The SEM-EDX investigation of the January 98 Composite sample also detected trace amounts of a number of other phases. These phases are Mg silicate, Fe-Ca-Al silicate-sulphate, K-Mg-Al silicate, Na-Mg-Al silicate, Ca-Na-Mg-Al silicate, K-Al silicate (feldspar) and $PbSO_4$.

Quantitative electron microprobe analyses were carried out on the As- and Sb-containing phases in the January 98 Composite sample, and the detailed analyses are presented in Appendix 2.

Table 3 summarizes the electron microprobe compositional data obtained for the major As_2O_3 phase. Thirty-nine particles of As_2O_3 were analyzed, and these particles included both the abundant tiny As_2O_3 crystals and the less common large masses of As_2O_3. Aside from its modest Sb content, the As_2O_3 is relatively pure, with only trace amounts of Fe and Pb being detected as impurities.

Its general formula is $(As,Sb)_2O_3$. Given the abundance of the As_2O_3 phase in this sample and its high As and Sb contents relative to the bulk composition of the dust (Table 2), it is clear that the As_2O_3 phase is the dominant As and Sb carrier in the January 98 Composite sample.

Table 3 - Electron Microprobe Determined Composition of the As_2O_3 Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
As	75.03	63.04 - 82.11
Sb	1.31	0.00 - 5.38
Fe	0.18	0.00 - 2.01
Pb	0.07	0.00 - 1.88

Table 4 presents the electron microprobe-determined compositional data for the Sb-rich oxide phase present in the January 98 Composite sample. Although this phase is a minor constituent of the dust, it has a high Sb and As content; that is, the phase is possibly best formulated as $(Sb,As)_2O_3$. The Sb-rich oxide seems to be relatively pure; only trace amounts of Fe and Pb are detected in its structure.

Table 4 - Electron Microprobe Determined Composition of the $(Sb,As)_2O_3$ Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
Sb	44.65	40.50 - 47.77
As	35.16	28.94 - 38.95
Fe	0.05	0.01 - 0.09
Pb	0.01	0.00 - 0.07

The January 98 Composite sample contains both an As-bearing iron oxide phase as well as an iron arsenate phase. Table 5 summarizes the compositional data obtained on nine particles of the As-bearing iron oxide. The iron oxide phase contains major amounts of Fe and O, in addition to minor contents of As and Sb, and traces of Pb and S. The compositional data suggest a hematite-like compound, but complementary structural studies would be needed to collaborate this conclusion. Table 6 summarizes the analogous data obtained from 16 particles of the iron arsenate phase. This material has a relatively low Fe content but relatively high levels of As and S, which likely are present as AsO_4 and SO_4. There are also trace amounts of Sb, Pb, Ca and Bi detected. The composition suggests an iron arsenate compound having a significant degree of sulphate substitution for arsenate, but it should be appreciated that some of the analyses may be biased by intimately admixed As_2O_3.

Table 5 - Electron Microprobe Determined Composition of the As-bearing Iron Oxide Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
Fe	59.11	57.51 - 61.11
As	4.68	3.15 - 5.87
Sb	1.67	1.15 - 2.10
Pb	0.10	0.05 - 0.17
S	0.04	0.00 - 0.08

Table 6 - Electron Microprobe Determined Composition of the Iron Arsenate Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
Fe	10.15	1.78 - 38.33
As	15.95	7.92 - 21.63
Sb	0.27	0.06 - 0.87
S	3.57	0.23 - 7.41
Pb	0.10	0.04 - 0.19
Ca	0.73	0.04 - 4.39
Bi	0.03	0.00 - 0.07

Characterization of the April 97 Composite Sample

In terms of its chemical composition (see Table 2), the April 97 Composite sample is similar to the January 98 Composite sample, although there are minor differences in the Sb contents as well as those of Fe, Al, Ca, Mg and Si. Both samples are more rich in As than the two samples collected from the storage chambers.

The SEM-EDX studies indicated many similarities between the April 97 Composite sample and the January 98 Composite sample. In this regard, Figure 8 shows the general appearance of the April 97 Composite sample as seen in a loose powder mount. The sample consists predominantly of 1-3 μm crystals of As_2O_3, many of which have well developed external octahedral crystal faces. The EDX analysis showed major amounts of As, together with traces of Sb. The larger, irregular particles are chlorite, which consists mostly of Fe, Mg, Al, Si and O. Comparison with Figure 2 indicates that the general morphologies of the April 97 Composite and January 98 Composite samples are very similar.

Figure 9 shows the April 97 Composite sample in more detail and in polished section. Most of the field consists of 1-3 μm crystals of As_2O_3, which generally occur free but sometimes are intergrown into larger agglomerates. The large, bright appearing particle in the centre of the image is $(As,Sb)_2O_3$ containing about 13% Sb. As noted above, the mechanism by which such large arsenic-antimony oxide particles form is not known. The figure also indicates a number of small particles of quartz that passed through the electrostatic precipitator circuit and were collected in the baghouse along with the As_2O_3.

Figure 10 shows an even larger mass of $(As,Sb)_2O_3$, the growth of which has sometimes encapsulated other species. Such large particles of $(As,Sb)_2O_3$ presumably formed on the walls or ducting of the baghouse where they accumulated to a considerable thickness before becoming dislodged and reporting with the baghouse dust. The large mass of $(As,Sb)_2O_3$ is associated with smaller crystals of As_2O_3, as well as with particles of quartz and chlorite. Notable is the presence of two ~10 µm particles of iron-calcium oxide containing only trace amounts of As or Sb. Figure 11 illustrates a ~5 µm compact particle of iron arsenate as well as a ~10 µm mass of $(As,Sb)_2O_3$, both of which are associated with 1-3 µm crystals of As_2O_3. Figure 12 illustrates a 10 µm zoned particle which was shown by EDX analysis to contain major amounts of Ca, As, S and O, as well as a trace amount of Fe. This phase is believed to be calcium arsenate-sulphate, and a number of such particles were identified in the April 97 Composite sample. The porous region of this figure is mounting medium.

In addition to the principal species discussed above, the detailed SEM-EDX studies identified trace amounts of K-Al silicate and Na-Al silicate; these phases likely represent fragments of different feldspars which passed through the electrostatic precipitator circuit into the baghouse. A few particles of calcium oxide containing trace amounts of Fe, As and Sb were also noted.

Quantitative electron microprobe analyses were carried out on the principal As- and Sb-containing phases in the April 97 Composite sample. The detailed electron microprobe results are presented in Appendix 3, and the analytical data are summarized below.

Twenty-four particles of the As_2O_3 phase were analyzed with the electron microprobe, and the results are summarized in Table 7. The material is relatively pure As_2O_3 which contains only 0.23% Sb, in addition to trace amounts of Fe, Pb, Ca and S. The Sb content of the dominant As_2O_3 phase in the April 97 Composite sample is lower than that of the As_2O_3 crystals in the January 98 Composite sample, despite the higher total Sb content of the April 97 Composite sample.

Table 7 - Electron Microprobe Determined Composition of the As_2O_3 Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
As	76.29	71.45 - 82.70
Sb	0.23	0.00 - 0.54
Fe	0.18	0.02 - 0.52
Pb	0.04	0.00 - 0.52
Ca	0.04	0.00 - 0.19
S	0.03	0.00 - 0.18

In addition to the "normal" As_2O_3 crystals, the April 97 Composite sample contains a number of arsenic oxide particles having an elevated Sb content, but not containing enough Sb to constitute $(Sb,As)_2O_3$. Eight of these Sb-rich As_2O_3 particles were analyzed with the electron microprobe, and the results are given in Table 8. The average Sb content is 13.55%, a high enough concentration to warrant the differentiation of this phase from the "normal" As_2O_3 crystals which contain only 0.23% Sb. A small amount of iron, along with traces of Pb, Ca, Bi and S, is also detected in this material.

Table 8 - Electron Microprobe Determined Composition of the Sb-rich As_2O_3 Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
As	59.59	50.84 - 68.70
Sb	13.55	12.14 - 15.09
Fe	0.42	0.07 - 1.62
Pb	0.05	0.00 - 0.15
Ca	0.13	0.00 - 0.21
Bi	0.01	0.00 - 0.03
S	0.05	0.00 - 0.21

The April 97 Composite sample contains an Sb-As oxide phase in which the amount of Sb equals or exceeds that of As; i.e., the phase has the general formula of $(Sb,As)_2O_3$. Thirty-two particles of the $(Sb,As)_2O_3$ phase were analyzed quantitatively with the electron microprobe, and the results are presented in Table 9. Comparison with the data of Table 4 suggests that the $(Sb,As)_2O_3$ phase in the April 97 Composite sample is very similar to that of the analogous phase in the January 98 Composite sample. In particular, the Sb and As contents of the $(Sb,As)_2O_3$ phase are virtually identical in the two samples.

Table 9 - Electron Microprobe Determined Composition of the $(Sb,As)_2O_3$ Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
Sb	44.55	42.43 - 46.72
As	35.94	30.71 - 42.45
Fe	0.14	0.00 - 0.84
Pb	0.06	0.00 - 0.34
Ca	0.01	0.00 - 0.11
S	0.84	0.50 - 1.23

The SEM-EDX studies identified both an iron arsenate phase and a calcium arsenate-sulphate phase having a high Sb content. Electron microprobe analyses of four grains of each phase were carried out, and the data are summarized in Table 10 and Table 11, respectively. The iron arsenate phase contains major amounts of both As and Sb, but has only a minor Ca and S content. This phase is clearly an iron arsenate-antimonate compound, although As always exceeds Sb in the structure. In contrast, the calcium arsenate-sulphate phase seems to have a major Sb content, but contains only minor amounts of Fe. It would be more accurately described as a calcium-iron sulphate-antimonate-arsenate.

Table 10 - Electron Microprobe Determined Composition of the Iron Arsenate Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
Fe	38.17	18.35 - 55.31
As	9.04	6.69 - 11.48
Sb	5.20	0.58 - 9.28
Pb	0.12	0.00 - 0.25
Ca	0.82	0.00 - 2.40
Bi	0.00	-
S	0.85	0.04 - 1.55

Table 11 - Electron Microprobe Determined Composition of the Calcium Arsenate-Sulphate Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range

Ca	11.47	10.22 - 12.26
Fe	2.24	1.91 - 2.55
Sb	15.43	11.15 - 20.28
As	8.46	7.73 - 9.57
S	8.93	7.41 - 9.89
Pb	0.14	0.12 - 0.16

A few particles of calcium oxide were detected during the SEM-EDX study of this sample, and four particles of this phase were analyzed by the electron microprobe. The results are given in Table 12. The phase is mostly calcium oxide, although there is a modest level of Fe present. Only minor amounts of As and Sb are detected. The low As and Sb contents, coupled with the rarity of this phase, make the calcium oxide a relatively unimportant carrier of either As or Sb in this sample.

Table 12 - Electron Microprobe Determined Composition of the Calcium Oxide Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
Ca	19.08	17.68 - 20.33
Fe	5.60	5.29 - 6.05
As	0.93	0.24 - 1.85
Sb	0.41	0.25 - 0.57
Pb	0.00	-
S	0.52	0.20 - 0.80

Characterization of the 212 Chamber Sample

Table 2 indicates that the 212 Chamber sample has the highest Si, Al, Ca, Mg and Fe contents of any of the dusts studied. Accordingly, it would be expected that this sample contains more of the silicate impurity species. The sample also has the highest Sb content of any of the samples, and should, therefore, contain more Sb-rich arsenic oxide species.

Figure 13 illustrates the general appearance of the 212 Chamber sample as seen in a loose powder mount. Most of the sample consists of 1-3 μm crystals of As_2O_3, and many of the crystals show the development of octahedral crystal faces. A number of somewhat larger silicate particles are present in this sample, and Figure 13 shows several such grains of chlorite and muscovite.

A detailed SEM-EDX study of the 212 Chamber sample was carried out using polished section mounts, and Figure 14 illustrates the general appearance of the sample. Most of the bright appearing grains in the photomicrograph are As_2O_3 or As_2O_3 having a modest Sb content. Most of the darker grey grains are chlorite or other silicate species, but some of these particles are As-bearing iron oxide or As-bearing calcium oxide containing a minor amount of Fe and traces of S and Si. Relative to the two more recently collected samples discussed above, the 212 Chamber sample has a higher Ca content (Table 2). Figure 15 provides another general view of the dust from the 212 Chamber. Although a number of tiny bright appearing crystals of As_2O_3 are evident, there are numerous darker appearing particles. Various fragments of quartz and chlorite are evident, as is the situation for all the samples studied. Numerous particles of iron arsenate occur, and these tend to be present as ~10 µm free grains. Of interest is a ~10 µm particle of As-bearing iron oxide that is rimmed very bright $(Sb,As)_2O_3$. A large grain of muscovite is rimmed by an Fe-Ca sulphate-arsenate phase. Relative to the initial two samples studied, there are more silicate and oxide particles present in the 212 Chamber sample, and several of these minerals seem to have undergone at least superficial alteration during roasting-gas cleaning.

Occasionally, large fragments of Sb-rich arsenic oxide or $(Sb,As)_2O_3$ are detected. Figure 16 illustrates one such occurrence. The bright appearing particle in the centre of the image has a high Sb content; it is likely $(Sb,As)_2O_3$. The particle is 20x40 µm in size. Such large particles were evident in the samples studied above, but the mechanism of formation of such large grains in the baghouse circuit is unknown. In Figure 16, the $(Sb,As)_2O_3$ particle is associated with tiny light grey crystals of As_2O_3 and slightly larger, and darker grey, particles of silicates and iron oxide or calcium oxide.

The 212 Chamber sample contains both iron arsenate and As-bearing iron oxide; the As-bearing iron oxide may be an intermediate phase in the formation of iron arsenate, although additional work would be required to substantiate this hypothesis. Figure 17 illustrates a large mass of iron arsenate, although smaller, typically ~10 µm particles, are more common. The large mass of iron arsenate seems to envelop smaller grains of As_2O_3, and the implication is that the iron arsenate mass "grew" in the baghouse system. In addition, there are two large grains of $CaSO_4$ evident in the image, and these particles reflect the fact that the dust in the 212 Chamber is more Ca-rich. Figure 18 illustrates a 10x12 μm particle of As-bearing iron oxide that may reflect an oxidized pyrite crystal. The grain is distinctly zoned and contains major Fe and O, with minor As and a trace quantity of Sb. Also shown is a smaller, dark appearing grain of As_2O_3 containing minor amounts of Fe and Sb that is probably a reaction product between fine iron oxide particles and the As_2O_3 crystals.

Quantitative electron microprobe analyses were carried out on the As- and Sb-bearing phases present in the 212 Chamber sample. The detailed analyses are presented in Appendix 4, and the results are summarized below.

Table 13 presents the average electron microprobe-determined composition of 31 As_2O_3 crystals present in the 212 Chamber sample. This oxide consists mostly of As, but contains a modest amount of Sb that is consistent with the bulk Sb content of this sample given in Table 2. In addition, there is a modest amount of Fe detected, as well as traces of Pb, Ca, Si and S; however, some of the detected impurity content could arise from secondary fluorescence from associated impurity phases. That is, the As_2O_3 crystals are so small that penetration by the electron beam is likely.

Table 13 - Electron Microprobe Determined Composition of the As_2O_3 Crystals in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
As	76.01	70.24 - 82.42
Sb	1.19	0.08 - 3.52
Fe	0.56	0.25 - 1.72
Pb	0.03	0.00 - 0.22
Ca	0.05	0.00 - 0.30
Si	0.05	0.00 - 0.52
S	0.04	0.00 - 0.15

In addition to the "normal" As_2O_3 crystals, which contain ~1% Sb, there are arsenic oxide particles which have elevated contents of Sb. In the January 98 Composite and April 97 Composite samples discussed above, the amount of Sb often exceeds that of As, such that the phase could be described as $(Sb,As)_2O_3$. In the 212 Chamber sample, the Sb content of the arsenic oxide, although significant, generally does not exceed that of As. Consequently the Sb-rich oxide in the 212 Chamber sample is best described as $(As,Sb)_2O_3$. Table 14 summarizes the electron microprobe data obtained on the $(As,Sb)_2O_3$ phase.

The material has a significant As and Sb content, and also contains trace amounts of Fe, Pb and S.

Table 14 - Electron Microprobe Determined Composition of the $(As,Sb)_2O_3$ Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
As	50.46	42.57 - 56.72
Sb	24.44	20.93 - 31.10
Fe	0.33	0.12 - 1.49
Pb	0.03	0.00 - 0.11
S	0.01	0.00 - 0.02

The 212 Chamber sample contains numerous ~10 µm particles of As-bearing iron oxide as well as an iron arsenate phase exhibiting a modest level of SO_4 substitution for AsO_4. The electron microprobe-determined composition of the As-bearing iron oxide phase, as based on the analysis of 16 particles, is given in Table 15, from which it is apparent that modest amounts of both As and Sb are incorporated in the iron oxide. Other impurity elements, including S, are present only in trace amounts. Table 16 summarizes the analogous compositional data for the iron arsenate phase, as based on the analysis of 21 particles of this material. The iron arsenate phase has a significant content of both Fe and As, and also contains a minor amount of S, which is probably present as SO_4 replacing AsO_4 in the iron arsenate structure. Significantly, there are only trace amounts of Sb and other impurity elements in this material.

Table 15 - Electron Microprobe Determined Composition of the As-bearing Iron Oxide in the 212 Chamber Sample (wt %)

Element	Average Composition	Range

Fe	52.41	44.90 - 57.53
As	8.54	3.51 - 14.88
Sb	3.09	0.77 - 9.89
Pb	0.38	0.16 -0.78
Ca	0.26	0.00 - 0.99
S	0.33	0.02 - 3.02

Table 16 - Electron Microprobe Determined Composition of the Iron Arsenate Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
Fe	12.60	11.34 - 13.21
As	31.67	26.19 - 37.33
Sb	0.49	0.38 - 0.73
Pb	0.72	0.50 - 1.10
Ca	0.86	0.64 - 3.46
S	1.58	1.12 - 2.21

The 212 Chamber sample contains a trace amount of an iron-calcium arsenate phase, and three particles of this compound were analyzed by the electron microprobe. As Table 17 indicates, this phase has a relatively low Sb content; it contains a minor amount of Pb as well as a trace of S.

Table 17 - Electron Microprobe Determined Composition of the Iron-Calcium Arsenate Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
Fe	6.62	5.08 - 9.59
Ca	3.03	2.03 - 4.12
As	35.21	29.93 - 41.34
Sb	1.09	1`.75 - 2.05
Pb	2.55	2.30 - 3.00
S	0.48	0.08 - 1.30

A few particles of a Ca-Fe-As oxide phase were detected in the 212 Chamber sample, and three of the particles were analyzed by the electron microprobe. Table 18 summarizes the data obtained, and shows that this oxide consists mostly of Ca, Fe and As, together with trace amounts of Pb, Sb and S. The iron-calcium arsenate phase and the Ca-Fe-As oxide phase are rare constituents of the 212 Chamber sample, and accordingly, are relatively unimportant overall As carriers despite their high As contents.

Table 18 - Electron Microprobe Determined Composition of the Ca-Fe-As Oxide Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
Ca	13.93	8.39 - 18.65
Fe	8.75	8.03 -9.93
As	10.75	1.38 -20.76
Sb	0.53	0.06 - 0.82
Pb	0.24	0.06 - 0.34
S	0.50	0.04 - 1.08

Characterization of the 236 Chamber Sample

Unlike the other three As_2O_3-rich dusts supplied, the 236 Chamber sample was slightly moist when received, and the water content must affect its analysis to some extent. Nevertheless, the compositional data of Table 2 suggest that the 236 Chamber sample is similar to that of the 212 Chamber material in that it has a comparatively low As content, together with high levels of Fe, Si, Al, Ca and Mg. The 236 Chamber sample has the lowest Sb content of the four samples studied. The implication is that this sample will contain an abundance of low-Sb As_2O_3 crystals and numerous silicate and oxide particles.

Figure 19 shows the general morphology of the 236 Chamber sample as examined in a loose powder mount. The material consists of abundant As_2O_3 crystals ranging in size from 1 µm to over 10 µm. The large size of some of the As_2O_3 crystals differentiates this sample from the others studied. In many instances, the As_2O_3 crystals have well developed external crystal faces, and the crystals are sometimes intergrown into small clusters. Various silicate species are detected in this sample, and Figure 19 shows a small particle of chlorite as well as a larger fragment of muscovite.

Figure 20 illustrates the general morphology of the 236 Chamber sample as seen in polished section. The bright particles are mostly crystals of As_2O_3, and these range in size from 1 µm to 10 µm. The darker appearing particles are mostly silicates, and these include quartz, chlorite and muscovite. Figure 21 shows two of the larger As_2O_3 crystals in greater detail, and also illustrates a

~10 µm particle of As-bearing iron oxide. Most of the dark appearing particles in the image are quartz, chlorite and muscovite. The large As_2O_3 crystals are somewhat porous and seem to be intergrowths of two or three individual crystals. The euhedral habit of the large As_2O_3 crystals suggests that they developed directly from the vapour phase, as the gas from the roaster circuit was cooled with dilution air.

Figure 22 illustrates a particle of As-bearing iron oxide as well as grains of quartz, chlorite and muscovite. The SEM-EDX analyses of the quartz detected only Si and O. Complementary quantitative electron microprobe analyses of three quartz particles indicated ~40% Si and ~59% O; only traces of K, Fe, Mg, Ca and Al were detected, and these trace impurity contents could originate from secondary fluorescence from closely associated impurity phases. Similar SEM-EDX analyses of the chlorite phase indicated Fe, Mg, Al, Si and O, together with occasional traces of K. Electron microprobe analyses of nine particles of the chlorite detected 13-18% Fe, 7-11% Mg, 6-11% Al and 7-11% Si. The composition, together with the X-ray diffraction analyses, indicates that the chlorite mineral is chamosite. The SEM-EDX analyses of the muscovite indicated major amounts of K, Al, Si and O, together with trace quantities of Mg and Fe. Quantitative electron microprobe analyses of five grains of this mineral found 3-7% K, 10-17% Al and 13-21% Si. The compositional range, together with the X-ray diffraction results, confirm the presence of muscovite rather than a potassium feldspar.

Various other species were also detected in trace amounts during the SEM-EDX study of the 236 Chamber sample. These species include iron arsenate, calcium arsenate containing only trace Fe, K-Na-Mg-Al silicate, Ca-Mg-Al silicate, Na-K-Al silicate, iron oxide containing minor Cr and As, apatite and pyrite.

The principal As- and Sb-containing phases in the 236 Chamber sample were analyzed quantitatively with the electron microprobe. The individual analyses are given in Appendix 5, and the various results are summarized below.

Table 19 summarizes the electron microprobe analyses of 60 particles of As_2O_3 in the 236 Chamber sample. The As_2O_3 contains a major amount of As, but only a trace quantity of Sb. The low Sb content is consistent with the low overall Sb content of this dust that is given in Table 2. There is also a trace amount of Fe present, but other impurities are nearly absent.

Table 19 - Electron Microprobe Determined Composition of the As_2O_3 Crystals in the 236 Chamber Sample (wt %)

Element	Average Composition	Range
As	76.78	71.43 - 79.87
Sb	0.19	0.00 - 0.99
Fe	0.27	0.08 - 1.13
Pb	0.02	0.00 - 0.13
Ca	0.01	0.00 - 0.09
Si	0.05	0.00 - 0.62
S	0.01	0.00 - 0.11

As noted above, a number of particles of As-bearing iron oxide are detected in the 236 Chamber sample, and 17 of these grains were analyzed quantitatively with the electron microprobe. Table 20 summarizes the results obtained. The iron oxide has a minor As content, but contains only a trace amount of Sb. Other impurity elements are detected only in low concentrations, but the presence of a small amount of Cr in the iron oxide in this sample is distinctive.

Table 20 - Electron Microprobe Determined Composition of the As-bearing Iron Oxide in the 236 Chamber Sample (wt %)

Element	Average Composition	Range
Fe	53.24	40.88-66.34
As	7.67	1.97 - 14.90
Sb	0.56	0.18 - 0.90
Pb	0.22	0.02 - 0.57
Ca	0.15	0.00 - 0.49
Cr	0.36	0.00 - 6.18
S	0.01	0.00 - 0.04

Comparison of the Four As_2O_3-Rich Dust Samples

From a mineralogical point of view, the four As_2O_3-rich dust samples are similar in that they contain, with only a few minor exceptions, the same species and in approximately the same amounts. These species are indicated qualitatively in Table 21. The two more recent samples, the January 98 Composite and the

April 97 Composite, have high As_2O_3 contents and contain relatively small amounts of the impurity silicate phases. In contrast, the two older samples from the storage caverns, 212 Chamber and 236 Chamber, have relatively high silicate contents that possibly reflect less than optimum functioning of the electrostatic precipitators at the time of their production. The Sb contents of the dusts vary from 0.3 to 2.13% Sb, and this variation affects the Sb content of the As_2O_3 crystals, as well as the amount and composition of the $(Sb,As)_2O_3$ phase present. In all cases, the dominant As carrier is As_2O_3, which normally occurs as tiny euhedral crystals, but sometimes is present as large irregular masses. A minor amount of the As is present as an Fe-bearing iron oxide or iron arsenate phase, in which the arsenic content varies from 1.9 to 38% As. The Ca arsenate or Ca-Fe arsenate phases are only minor As carriers in any of the dust samples. Most of the Sb in the samples is present in solid solution in the As_2O_3 crystals. The Sb content of the As_2O_3 varies from 0% to 47%. The more Sb-rich compositions are actually $(Sb,As)_2O_3$, and this phase often occurs as large irregular masses. A minor amount of the total Sb substitutes for As in the iron arsenate phase, and traces of Sb occur in the Ca arsenate, Ca-Fe arsenate and Fe arsenate-sulphate phases. Unlike As and Sb, most of the iron in the samples occurs in silicate form (chlorite) and as iron oxide. Lesser amounts of the total iron are present as iron arsenate or Ca-Fe arsenate, which contains 5-10% Fe.

Table 21 - Qualitative Comparison of the Phases Present in the Four As_2O_3-rich Dust Samples

Species	January 98 Composite	April 97 Composite	212 Chamber	236 Chamber
As_2O_3	major	major	major	major
Fe arsenate	minor	minor	minor	minor
$(Sb,As)_2O_3$	minor	minor	minor	trace
Ca-Fe arsenate	trace	trace	minor	trace
Fe arsenate-sulphate	trace	trace	trace	very rare
Iron oxide	trace	trace	trace	trace
Ca-Fe oxide	very rare	trace	trace	very rare
Ca sulphate	very rare	very rare	trace	very rare
Chlorite	minor	minor	minor	minor
Quartz	trace	trace	trace	trace
Muscovite	minor	minor	minor	minor

Solubility Measurements

The aqueous solubility of two lots of reagent grade As_2O_3 was determined over the temperature range from 20°C to 100°C. The results obtained are presented graphically in Figure 23 and Figure 24, and the detailed numerical data are given in Appendix 6. For the first sample, the results obtained on heating and cooling are identical, and the implication is that the measured values reflect the true equilibrium solubility of As_2O_3 in water. This conclusion is further supported by the close agreement of the current data with the published values of the solubility of As_2O_3 in water reported by Linke and Seidell (2). The results obtained for the second lot of reagent grade As_2O_3 are slightly higher at the higher temperatures and, for this sample, there is a slight difference between the heating and cooling data at the lower temperatures. This may indicate that the lower temperature values are not truly saturated, despite the fact that equilibration periods of ~3 days were used. X-ray diffraction analysis of the solids in equilibrium with the solution at different temperatures indicated only the cubic arsenolite form of As_2O_3.

The oxidation state of the dissolved arsenic generated from the first lot of reagent grade As_2O_3 was determined by ion chromatography, and the detailed results are also presented in Appendix 6. At all temperatures, and on heating and cooling, only trace amounts of As(V) were detected. In fact, the concentration of As(V) never exceeded 0.1 g/L As(V), despite the fact that total arsenic concentrations as high as 63 g/L As were generated during the solubility measurements. Virtually all of the arsenic is present in the trivalent form; i.e., as As_2O_3, and the As(III) does not oxidize to any significant extent throughout the solubility measurements, which commonly lasted for over 30 days.

The solubility of reagent grade Sb_2O_3 was also measured to provide a comparison with the analogous data for As_2O_3. The results for the solubility of Sb_2O_3 in water are summarized graphically in Figure 25, and the numerical data are presented in Appendix 6. Unlike As_2O_3, which enjoys a moderate solubility in water, Sb_2O_3 is nearly insoluble over the entire temperature range from 25 to 95°C. The solubility at 25°C is <10 mg/L, and even at 95°C, it is only 55 mg/L Sb_2O_3. The data reveal a small difference between the solubilities measured on heating and those determined on cooling. Although the measured differences of <10 mg/L Sb_2O_3 could be due to analytical error at the low concentrations involved, equally they could reflect the partial oxidation of Sb(III) to Sb(V) during the course of the experiments or the tendency of the dilute Sb_2O_3-containing solutions to supersaturate on cooling . In any event, it is clear that the solubility of Sb_2O_3 is at least three orders of magnitude lower than that of As_2O_3. This conclusion is also supported by the limited solubility data published for Sb_2O_3 in water. For example, Linke and Seidell (2) report that the solubility of Sb_2O_3 is only 8.4 mg/L at 25°C, a value in general agreement with the results of this study. The inference is that the presence of even very modest amounts of Sb_2O_3 in solid solution in As_2O_3 will significantly reduce the solubility of the arsenic oxide.

The solubility of As_2O_3 over the four As_2O_3-rich dust samples was measured as a function of temperature on heating and cooling. The results are displayed graphically in Figures 26, 27, 28 and 29, and the detailed numerical data are presented in Appendix 6. The graphs also present the measured solubility of As over reagent grade As_2O_3 for comparative purposes.

In all instances, the solubility of As_2O_3 over the As_2O_3 rich dust, measured on heating, is much lower than that determined over reagent grade As_2O_3. In fact, the solubility of As_2O_3 over the dust at any temperature during the heating cycle is about one-half of that over reagent grade As_2O_3, despite the fact that a 2½ -3 day equilibration period was employed at each temperature. Furthermore, there is a pronounced hysterisis between the data obtained on heating and those realized on cooling. The solubility increases systematically as the temperature is increased from 5°C to ~95°C. As the temperature is reduced, however, the solubility of As_2O_3 remains nearly constant until the solubility curve for reagent grade As_2O_3 is intersected. As the temperature is reduced further, the solubility curve then follows that of the reagent grade As_2O_3.

The solubilities of Sb over the As_2O_3-rich dusts were also measured as a function of temperature on heating and cooling. The individual solubility curves for the four As_2O_3-rich dust samples are presented in Figures 30, 31, 32 and 33; the detailed solubility data are given in Appendix 6. The measured solubilities of Sb are low at all temperatures studied; even at 95°C, the solubility is always less than 160 mg/L Sb. In many instances, the solubility of Sb over the As_2O_3-rich dust is greater than that over reagent grade Sb_2O_3. One possible explanation is that part of the Sb in the As_2O_3-rich dust is present as Sb(IV) or Sb(V) rather than as

Sb(III), which is present in Sb_2O_3. The solubility data on cooling are consistently higher than the values realized on heating, and this trend could indicate some oxidation of the Sb during the experiments, although it could equally well be caused by the slow crystallization (i.e. supersaturation) of the low concentrations of dissolved Sb(III) throughout the cooling cycle.

Although the measured solubility of As_2O_3 over reagent grade As_2O_3 is similar to the accepted value reported in the literature (2), the solubility of As_2O_3 over the four As_2O_3-rich dust samples is much lower than that expected from the bulk composition of the dusts, which have an abundance of As_2O_3. One possible cause of the lower than expected solubilities could be a very slow rate of dissolution of As_2O_3 from the dusts. To pursue this possibility, the solubility of reagent grade As_2O_3 was measured as a function of time at 25°C and 60°C, and that of the 212 Chamber sample was measured at 95°C. The results are summarized in Figures 34 and 35, respectively. Reagent grade As_2O_3 dissolves slowly, and at 25°C, ~70 h (3 days) is needed to achieve the equilibrium solubility. At 60°C, the time to reach saturation is about 24 h. The As_2O_3 dissolves relatively rapidly from the 212 Chamber sample at 95°C. Only about 8 h is needed to reach a steady state As_2O_3 concentration, which does not vary significantly for more extended heating times up to 170 h. As indicated by Figure 28, however, the solubility realized over the 212 Chamber sample is not that of pure As_2O_3, despite the constancy of the value. Because equilibration times of 2 ½-3 days were used in the present experiments, and even longer times were employed at temperatures lower than 30°C, the duration of the equilibration period at each temperature is not likely the cause of the low As_2O_3 solubilities over the As_2O_3-rich dust samples.

Additional support for this conclusion is provided by the data given in Table 22 that show the concentrations of As(III) and As(V) in the solutions in contact with the four As_2O_3-rich dust samples as a function of time. Clearly, the As concentration (as reflected by the sum of As(III) and As(V)) does not increase to any significant extent with increasing equilibration times, even for periods as long as 21 days.

Another possible cause of the lower solubility of arsenic from the As_2O_3-rich dust samples could be an enhanced rate of oxidation of As(III) in the presence of the diverse solid species in the dust. To evaluate this possibility, the As_2O_3-rich dust samples were equilibrated with water at room temperature for times up to 21 days, about two-thirds of the total duration of the individual solubility tests. Samples were taken periodically and the solutions were analyzed for As(III) and As(V) using liquid chromatography. The results, which are summarized in Table 22, indicate that the concentration of As(V) is always less than 5% of the total As concentration, and that the As(V) concentration does not increase in any significant way with increasing retention time in the presence of water, air and the various solid phases contained in the dust. Clearly, the oxidation of the dissolved arsenic is not the cause of the lower than expected As_2O_3 solubilities from the As_2O_3-rich dust samples.

Table 22 - Concentrations of As(III) and As(V) in the Saturated Solutions Generated From the As_2O_3-rich Dust Samples

Sample	Temperature (°C)	Time (days)	As(III) (g/L)	As(V) (g/L)
January 98	26.3	7	9.02	0.07
Composite		9	9.06	0.07
		21	9.55	0.08
April 97	26.4	7	13.7	0.07
Composite		9	13.7	0.07
		21	13.8	0.09
212 Chamber	23.4	7	9.13	0.30
		9	9.09	0.30
		21	9.48	0.32
236 Chamber	26.6	7	13.9	0.33
		9	13.9	0.32
		21	14.3	0.34

The above discussion suggests that the low As_2O_3 solubility from the As_2O_3-rich dust samples is an inherent property of the dust itself, and is not a consequence of the measuring technique. Further support for this hypothesis comes from Figure 36 which compares the As_2O_3 solubilities over the four As_2O_3-rich dust samples, as obtained on heating only. Although all the solubilities are low relative to that of reagent grade As_2O_3, there are significant solubility variations among the four As_2O_3-rich dust samples themselves. There is some indication that the observed solubility differences are related to the total Sb content of the dust, and possibly, to the solid solution Sb content of the As_2O_3 crystals present in the dust. In this regard, Figure 37 shows the As_2O_3 solubility at 65°C and 95°C as a function of the total Sb content of the dust for the four As_2O_3-rich dust samples (Table 2), as well as for reagent grade As_2O_3. These solubilities were calculated by fitting the experimental solubility data, obtained on heating, to a second order polynomial equation of the form:

$$\text{Solubility (g/L } As_2O_3) = a + bt + ct^2 \qquad (1)$$

where t is the temperature in °C. The relevant equations are given below.

Reagent Grade As_2O_3: $S = 14.78 + 0.0626\ t + 0.00649\ t^2$ (2)

January 98 Composite: $S = 5.41 + 0.1094\ t + 0.00223\ t^2$ (3)

April 97 Composite: $S = 6.12 + 0.2012\ t + 0.00123\ t^2$ (4)

212 Chamber: $S = 6.31 + 0.0888\ t + 0.00167\ t^2$ (5)

236 Chamber: $S = 9.77 + 0.2414\ t + 0.00151\ t^2$ (6)

The data given in Figure 37 suggest that the solubility of As_2O_3 is related to the Sb content, and that small amounts of Sb have a significant effect on the solubility of

As_2O_3. In this regard, a similar trend is observed when the solubility of As_2O_3 is plotted against the solid solution Sb content of the As_2O_3 crystals in the four As_2O_3-rich dust samples (see Figure 38). Presumably, the presence of Sb in the As_2O_3 crystals causes a significant reduction in the thermodynamic activity of As_2O_3 that, in turn, results in a reduction in the aqueous solubility of the oxide. Based on the data presented in Figures 37 and 38, the effect is most pronounced for Sb contents in the 0.0 - 0.5% Sb range, but more experimentation would be required to substantiate this hypothesis.

The mineralogical characterization studies of the four As_2O_3-rich dust samples showed that the dominant As_2O_3 phase has solid solution Sb contents ranging from zero to several percent. Based on the hypothesis that only the low-Sb As_2O_3 crystals dissolve readily, the addition of greater amounts of solid As_2O_3-rich dust should increase the measured solubility of As_2O_3 over the dust. That is, the addition of a significant excess of dust to the solubility vessel consequentially results in the addition of more low-Sb As_2O_3 to the system. The low-Sb As_2O_3 is postulated to dissolve readily, and should, therefore yield higher As_2O_3 solubilities over the dust. To test this hypothesis, various amounts of the April 97 Composite sample were added to 1L of water heated to 70°C in a 2-L solubility reactor (see Figure 1). After 96 h of agitation at 70°C, the solution was sampled, diluted and analyzed for As and Sb. The results of this part of the investigation are summarized in Table 23. When an initial pulp density of 75 g/L solids was employed, the measured solubility over the April 97 Composite sample was 41.55 g/L As_2O_3. It is important to recognize that, based on the overall composition of the April 97 Composite sample presented in Table 2 and assuming that all of the contained As is present as As_2O_3, an initial pulp density of 75 g/L corresponds to 130% of the As_2O_3 required to achieve the ~51 g/L As_2O_3 solubility of reagent grade As_2O_3 at 70°C. Increasing the pulp density to 150 g/L solids yields a solubility of 48.03 g/L As_2O_3, and a pulp density of 300 g/L gives a solubility of 51.76 g/L As_2O_3. The latter value is essentially that of reagent grade As_2O_3 at 70°C (50.96 g/L As_2O_3). The implication is that a large excess of the solid As_2O_3-rich dust will result in an As_2O_3-saturated solution, even during the heating cycle. In contrast, the Sb concentration of the solution appears to be nearly independent of the pulp density, and this implies the rapid saturation of all the solutions with respect to Sb.

Table 23 - The Aqueous Solubility of As_2O_3 and Sb at 70°C for Various Initial Pulp Densities of the April 96 Composite Sample

Pulp Density (g/L)	Solubility of As_2O_3 (g/L)	Solubility of Sb (mg/L)
75	41.55	41
150	48.03	37
225	48.87	34
300	51.76	37
Reagent Grade As_2O_3	50.96	-

Support for the hypothesis that only the low-Sb As_2O_3 crystals dissolve readily at temperatures below 100°C comes from the mineralogical characterization of the leach residues from the above experiments done at various initial pulp densities. Figure 39 illustrates the general morphology of the leach residue from the test done using an initial pulp density of 75 g/L, and Figure 40 shows the morphology of the analogous residue from the experiment done using an initial pulp density of 150 g/L of the April 97 Composite sample. Both residues consist of tiny particles of As_2O_3 having a low but detectable Sb content, and of larger bright appearing particles of $(Sb,As)_2O_3$. The darker appearing grains are chlorite, muscovite, quartz, iron oxide and iron arsenate. Relative to the unleached material (see Figures 9 and 11), the As_2O_3 crystals in the water-leached residues are significantly reduced in size. This reduction in particle size is believed to result from the rapid dissolution of the low-Sb As_2O_3 crystals. In contrast, the $(Sb,As)_2O_3$ particles appear to have the same size and morphology as they possessed in the original sample. Of course, water leaching does not affect the morphology of the silicate species.

Quantitative electron microprobe analyses of the As_2O_3 crystals remaining in the water leach residues were carried out. All the data are presented in Appendix 7, and the results are summarized in Table 24. The As_2O_3 crystals in the as-received April 97 Composite sample have a solid solution Sb content of 0.238%. Leaching of this sample at 70°C and at an initial pulp density of 150 g/L solids (i.e., with a ~250% excess of the As_2O_3-rich dust), results in an increase in the average solid solution Sb content of the As_2O_3 crystals to 0.819%. When an initial pulp density of 75 g/L solids was employed, the residual As_2O_3 crystals have an average Sb content of 1.64%. The implication is that the low-Sb As_2O_3 crystals dissolve readily. As the dissolution of the As_2O_3 proceeds, the Sb content rises in the residual particles and, eventually, the Sb content impedes the dissolution reaction. This trend is also reflected in the expanded range of the Sb contents of the As_2O_3 crystals in the leach residues, especially that from the 75 g/L pulp density experiment.

Table 24 - Electron Microprobe Determined Composition of the As_2O_3 Crystals After Leaching at Various Initial Pulp Densities and at 70°C (wt %)

Condition	Average As Content	Range	Average Sb Content	Range
April 97 Composite sample	76.29	71.45-82.70	0.238	0.000-0.545
150 g/L Solids Leach	74.63	70.48-83.33	0.819	0.122-4.254
75 g/L Solids Leach	74.77	70.20-81.82	1.648	0.279-7.445

High Temperature Leaching of the As_2O_3-Rich Dusts

The experiments presented above indicate that the As_2O_3-rich dusts from the Giant Mine do not dissolve extensively in water at temperatures <100°C. Although the concentration of dissolved arsenic over the four As_2O_3-rich dusts is relatively low, it increases systematically with increasing temperature. Accordingly, the use of temperatures >100°C should generate a more concentrated As_2O_3 solution, and this option was investigated using an autoclave at 125-200°C.

Table 25 shows the As_2O_3 aqueous solubilities achieved when ~100 g/L of each of the four As_2O_3-rich dusts was heated in water in an autoclave for 2 h at 125, 150, 175 and 200°C, followed by cooling to 95°C and sampling. Initially heating the As_2O_3-rich dusts to 125-200°C results in a significant increase in the As_2O_3 solubility at 95°C, and in this regard, it should be recalled that the apparent solubility achieved by heating any of the dusts directly to 95°C is only ~45 g/L As_2O_3. Heating of the As_2O_3-rich dusts to 125°C, followed by cooling to 95°C, results in a significantly enhanced solubility relative to the solubility values realized by directly heating the slurries to 95°C. Heating to a higher temperature results in a further As_2O_3 solubility increase for the April 97 Composite and the 212 Chamber samples, but has little effect on the solubility of the January 98 Composite or 236 Chamber samples. The 212 Chamber sample seems to reach saturation at 150°C, and both the January 98 Composite and 236 Chamber samples give As_2O_3-saturated solutions after heating to only 125°C.

Table 25 - Solubility of As_2O_3 in Water at 95°C After a Two-hour Heating Period at Elevated Temperatures in an Autoclave (g/L As_2O_3)

Sample	Heating Temperature			
	125°C	150°C	175°C	200°C
January 98 Composite	87.1	79.7	80.9	83.8
April 97 Composite	73.9	73.9	82.6	87.1
212 Chamber	67.4	81.2	80.6	80.2
236 Chamber	85.1	84.9	80.8	81.6

Based on the data given in Table 25, the procedure outlined in Figure 41 was developed to produce a significant yield of "pure" As_2O_3 crystals by hot water leaching of the As_2O_3-rich dusts. The procedure consists of leaching the As_2O_3-rich dusts in water, in an autoclave, for 2 h at 150°C and under the "neutral" atmosphere generated by the air in the vessel plus the significant steam pressure produced at the leaching temperature. After 2 h of leaching at the elevated temperature, the slurry was cooled to 95°C, and was filtered while hot. The clear, As_2O_3-saturated liquor was then cooled to room temperature to crystallize As_2O_3. An autoclave temperature of 150°C was employed, but it is possible that further test work could reduce this temperature somewhat, at least for some of the As_2O_3-rich dust samples. Also, additional refinement of the procedure possibly could shorten the time needed to achieve As_2O_3 saturation at the elevated temperatures used.

Table 26 summarizes the results obtained when the four As_2O_3-rich dust samples were leached at 150°C using the procedure given in Figure 41 and at various initial pulp densities. For any of the samples, decreasing the initial pulp density results in a higher dissolution of As_2O_3 from the dust, and a lower As content in the leach residue. The maximum extraction of 93% was achieved using 48 g/L of the January 98 Composite sample, and the lowest extraction of 75% was obtained when 91 g/L of the 212 Chamber sample was treated. For any of the samples, a relatively constant level of As_2O_3 dissolution is achieved for initial pulp densities up to ~80 g/L, but the extractions decrease at still higher pulp densities. Clearly, the decreasing solubility reflects the point at which an As_2O_3-saturated solution is produced; any additional As_2O_3-rich dust simply accumulates in the leach residue, thereby lowering the total percentage of As_2O_3 dissolved. Impurities, such as Fe, Sb and Au accumulate in the residue as the As_2O_3 dissolves, and this observation is consistent with the low water solubility of these species. The Au content of most of the leach residues is commercially interesting.

Following filtration at ~95°C, the clear filtrates were cooled to room temperature, while being gently stirred, to crystallize a pure As_2O_3 product. The resulting crystals were filtered and then dried in an oven at 110°C. The crystals were weighed to give the yield of product, and were analyzed for As, Sb and Fe. As shown in Table 27, the yield of product depends on the degree of saturation at 95°C, which in turn depends on the initial pulp density employed in the leaching stage at 150°C. The experiments done using high initial pulp densities produce nearly saturated solutions at 95°C, and in turn, these result in high yields of the As_2O_3 product. Comparison with Table 26, however, shows that the tests done at high pulp densities also result in relatively low overall levels of dust dissolution. In practice, it will be necessary to strike a compromise between the pulp density needed to give a high level of dust dissolution and that required to produce a highly concentrated As_2O_3 solution at 95°C. Because, in any commercial process, the cold As_2O_3-bearing solution from the crystallization of the As_2O_3 product would likely be recycled as "water" to the pressure leaching stage, the optimum initial pulp density should be re-determined using recycled As_2O_3-bearing solutions.

Table 26 - Results Obtained by Leaching the As_2O_3-rich Dusts for 2 h at 150°C, Followed by Cooling and Filtration at ~95°C

Sample	Initial Pulp Density (g/L)	Dust Dissolved (%)	Residue Composition (%)			
			As	Sb	Fe	Au (ppm)
January 98 Composite	104	85.7	34.5	3.3	10.1	25.9
	95	88.5	23.7	6.4	12.4	37.6
	85	91.2	14.5	3.8	15.8	40.1
	71	91.3	14.1	4.7	16.2	39.2
	60	91.2	12.4	5.0	16.3	40.1
	50	93.0	9.4	3.0	17.1	43.4
April 97 Composite	85	91.1	25.1	15.1	9.4	29.9
	76	91.7	23.7	13.8	9.7	32.0
212 Chamber	113	77.4	21.4	7.4	14.2	54.7
	100	75.5	18.7	7.5	15.0	56.6
236 Chamber	100	88.4	11.6	1.3	17.7	57.4
	90	89.0	8.4	1.1	18.0	43.9

The As_2O_3 crystals produced on cooling were shown by X-ray diffraction analysis to consist only of the cubic arsenolite form of As_2O_3; no other phases were detected. The As_2O_3 was generally of high chemical purity; in many cases the product consisted of >99% As_2O_3. Contamination of the As_2O_3 with Sb or Fe was generally low, except for those experiments where the leach solution was not saturated with As_2O_3. In many of the experiments, the Sb content of the As_2O_3 crystals was <0.2% and the Fe content was <0.005%. Hence, it is believed that the high temperature leaching procedure outlined in Figure 41 could yield a commercially acceptable As_2O_3 product.

Table 27 - Arsenic Concentrations of the Solutions and the Purity of the As_2O_3 Crystals Made Using the High Temperature Leaching Procedure

Sample	Initial Pulp	[As]	[As]	As_2O_3 Crystals

	Density (g/L)	at 95°C (g/L)	at 25°C (g/L)	Yield (g/L)	As_2O_3 (%)	Sb (%)	Fe (%)
January 98	104	59.7	17.4	57.7	98.3	0.06	0.003
Composite	95	59.0	21.0	52.5	95.8	0.03	0.005
	85	54.9	18.5	48.9	99.9	0.07	0.002
	71	46.0	17.7	37.4	99.1	0.16	0.001
	60	39.2	16.7	30.6	99.5	0.28	0.002
	50	28.5	22.0	9.7	97.9	0.97	0.005
April 97	85	62.8	21.5	51.1	98.7	0.11	0.008
Composite	76	56.5	19.3	47.3	97.7	0.13	0.008
212	113	55.8	19.4	47.5	98.3	0.06	0.008
Chamber	100	49.5	16.8	47.4	99.0	0.10	0.008
236	100	61.0	18.6	50.9	97.7	0.18	0.004
Chamber	90	50.2	16.6	44.6	99.0	0.22	0.002

In the hot water leaching procedure illustrated in Figure 41, the arsenic is distributed among the As_2O_3 crystals, the high temperature leach residue and the cold solution. Mass balances were carried out to determine the relative distribution of arsenic among the three phases, and the results are given in Table 28. Only 1-9% of the total arsenic remains in the high temperature leach residue, and the amount of residual arsenic increases as the initial pulp density increases. For the preferred range of initial pulp densities likely to be used in a commercial process, however, the amount of residual arsenic seems to be only 2-4% of the total. Under the same preferred pulp density conditions, about 25-30% of the total arsenic remains in the cold solution. In a commercial application, however, this solution would almost certainly be recycled as "water" for the high temperature leaching in operation. Hence, negligible amounts of the total arsenic leached in subsequent cycles would report to the cold solution in a continuous operation. Accordingly, it can be concluded that 96-98% of the total arsenic would report as As_2O_3 crystals in a commercial hot water leaching process wherein the cold solution after As_2O_3 crystallization was recycled.

Table 28 - Relative Arsenic Distribution in the Hot Water Leaching Procedure

Sample	Initial Pulp Density (g/L)	Relative Arsenic Distribution

		In Leach Residue (%)	In Cold Solution (%)	In As_2O_3 Crystals (%)
January 98 Composite	104	7.3	25.3	67.4
	95	3.9	32.4	63.7
	85	1.8	30.9	67.3
	71	1.8	36.2	62.0
	60	1.6	39.8	58.6
	50	1.0	64.8	34.2
April 97 Composite	85	2.9	32.7	64.3
	76	2.6	32.8	64.6
212 Chamber	113	8.5	30.9	60.6
	100	7.5	28.1	64.4
236 Chamber	100	2.2	27.0	70.8
	90	1.5	30.8	67.6

Mineralogical Characterization of the Hot Water Leach Residues

Samples of the four As_2O_3-rich dusts were leached for 2 h at 150°C, at various initial pulp densities, as noted above. The slurry was rapidly cooled in the autoclave to 95-100°C, and the vessel was then opened. The hot slurry was filtered, and the solids were washed with a small amount of water to displace the nearly As_2O_3-saturated processing solution. The leach residues were water washed and dried at 110°C for a few hours prior to mineralogical study.

X-ray diffraction analysis of the residue from the leaching of the January 98 Composite sample, obtained using an initial pulp density of 95 g/L solids, indicated an As_2O_3-type compound, quartz, chlorite, muscovite and traces of other unidentifiable species. Similar X-ray diffraction analyses of the April 97 Composite sample leached at an initial pulp density of 77 g/L or 85 g/L solids detected an As_2O_3-type compound, quartz, chlorite, muscovite, hematite and other unidentifiable phases.

The SEM-EDX studies of the latter two samples provided complementary mineralogical information and phase confirmation. Figure 42 shows the residue from the leaching experiment done using an initial pulp density of 77 g/L solids. The bright appearing grains are rich in both Sb and As; they are $(Sb,As)_2O_3$, which is likely the As_2O_3-type compound identified by X-ray diffraction analysis. Relative to the $(Sb,As)_2O_3$ particles in the as-received As_2O_3-rich dust, the

$(Sb,As)_2O_3$ particles in the leach residue are better crystallized. In fact, many of the particles show well developed external crystal forms, possibly indicating the localized dissolution-crystallization of the $(Sb,As)_2O_3$ phase. The low-Sb As_2O_3 crystals prevalent in the as-received As_2O_3-rich dust are lacking, and this behaviour is not unexpected given the low pulp density used for this leaching experiment. The various dark appearing grains are mostly chlorite, muscovite or quartz, although a number of fragments of As-bearing iron oxide are also detected. Figure 43 shows the analogous leach residue from the experiment done using an initial pulp density of 85 g/L solids; the leach residue contains 25.1% As, 15.1% Sb and 9.4% Fe. Most of the bright appearing particles are crystals of $(Sb,As)_2O_3$, whereas the darker appearing particles are chlorite, muscovite, quartz and As-bearing iron oxide. Both figures suggest that the low-Sb As_2O_3 crystals dissolve during hot water leaching. In contrast, the Sb-rich oxides, iron oxides and silicate species are poorly soluble and accumulate in the leach residue.

X-ray diffraction analyses were also carried out on the residues from the water leaching of the 212 Chamber sample for 2 h at 150°C. The residues were generated for initial pulp densities ranging from 100 to 113 g/L, but all the residues were virtually identical. They consist of an As_2O_3-type compound (likely $(Sb,As)_2O_3$), chlorite, muscovite, quartz and iron oxide (hematite).

Removal of Antimony from the Water Leach Solutions

Preliminary research on the water leaching option was carried out by Royal Oak Mines. In their studies, leaching was done at 100°C, and it is now known that such temperatures yield low concentrations of dissolved As_2O_3. In the Royal Oak work, the solution was evaporated to ~30% of its volume to increase the concentration of As_2O_3, and the evaporated solution was cooled to crystallize As_2O_3. In the Royal Oak work, the crystals contained 99.6% As_2O_3, 0.33% Sb and 0.08% Fe. The Sb content was considered to be excessive, and accordingly, tests were done to remove the Sb from solution using either ion exchange or activated carbon. Those experiments, however, were inconclusive, and accordingly, additional work was done at CANMET on the use of ion exchange resins or activated carbon for antimony control.

Table 29 illustrates the composition of a solution which was made by leaching 100 g/L of the 212 Chamber sample with hot water at 100°C. The hot slurry was filtered, and the filtrate was analyzed. The solution was then cooled to room temperature and was held at room temperature for 72 h. The Sb concentration at 90°C is about that expected from the measured solubility data (Figure 32), but the solubility decreases significantly as the temperature is lowered. The measured concentration of Sb at 25°C is about three times greater than the reported solubility of antimony at 25°C which is 0.0084 g/L Sb_2O_3 (5). It is not known whether this discrepancy is due to the presence of some Sb(V) in the 212 Chamber sample, or whether it reflects a persistent level of Sb_2O_3 supersaturation in water. The latter explanation may be more likely as it was noted that the Sb_2O_3 tended to remain in solution, in a supersaturated state, for several hours when the solution was cooled from 90°C to 25°C.

Table 29 - Composition of the Solution Resulting From the Hot Water Leaching of the 212 Chamber Sample

Time (h)	Temperature (°C)	As Concentration (g/L)	Sb Concentration (g/L)
0	90	24.5	0.0643
24	25	21.0	0.0272
72	25	21.4	0.0263

The data of Table 30 show the Sb concentrations resulting when the As_2O_3-rich dust samples were subjected to the hot water leaching procedure (Figure 41) for 2 h at 150°C, and were then cooled to 95°C and subsequently to room temperature. The Sb concentrations in the 95°C solutions vary widely, and seem to depend on both the dust sample used and its pulp density. There is an inverse correlation between the Sb and As concentrations of the hot solution, although the correlation is not precise. The Sb concentration of the solutions cooled to 25°C varies widely, from 0.029 to 0.194 g/L Sb. This observation could reflect the presence of variable amounts of Sb(V) in the dust samples, or more likely, an erratic level of Sb_2O_3 supersaturation in the cooled solutions. In any event, a modest amount of Sb dissolves along with the As_2O_3, and the Sb persists in solution at room temperature.

Table 30 - Antimony Concentrations Produced in the Hot Water Leaching Procedure

Sample	Initial Pulp Density (g/L)	Sb Concentration at 95°C (g/L)	As Concentration at 95°C (g/L)	Sb Concentration at 25°C (g/L)
January 98	104	0.075	59.7	0.030
Composite	95	0.094	59.0	0.093
	85	0.113	54.9	0.081
	71	0.139	46.0	0.086
	60	0.154	39.2	0.080
	50	0.130	28.5	0.048
April 97	85	0.130	62.8	0.075
Composite	76	0.118	56.5	0.068
212 Chamber	113	0.191	55.8	0.181
	100	0.171	49.5	0.194
236 Chamber	100	0.121	61.0	0.029
	90	0.134	50.2	0.049

Although Royal Oak Mines reported some success in removing Sb from the water leach solutions using the Gravex GR-2-0 ion exchange resin or activated carbon, their results might simply reflect the delayed crystallization of the antimony on the surface of the resin or carbon during the cooling of the solutions in their experiments. In an effort to confirm the preliminary results obtained by Royal Oak Mines, the removal of Sb was studied using the four ion exchange resins presented in Table 1 as well as Hycarb 6x12 activated carbon. As shown in Table 31, however, none of the resins extracted any significant amount of Sb from the water leach solutions at room temperature and their natural pH of ~6. For these experiments, the 212 Chamber sample was leached at 95°C in water for several hours to generate an As- and Sb-bearing solution. The leach slurry was filtered and then was cooled to room temperature for ~24 h. The cooled solution analyzed 21 g/L As and 0.0263 g/L Sb. One hundred millilitre samples of the cooled solution were contacted with 2 mL of the various resins, and the mixtures were gently agitated overnight at room temperature using an orbital shaker. The solutions were then analyzed for As and Sb; the results are summarized in

Table 31. None of the resins is effective for extracting Sb from the water leach solution; less than 10% of the total Sb was removed in any of the experiments.

Table 31 - Concentrations of As and Sb After Prolonged Contact With Different Ion Exchange Resins at Room Temperature

Resin	As Concentration (g/L)	Sb Concentration (g/L)
Feed solution	21	0.0263
Gravex GR-2-0	21	0.0247
Amberlite IRC-120	21	0.0266
Amberlite IRC-50	21	0.0249
Duolite C-467	21	0.0232

Efforts were also made to extract the Sb from a hot aqueous leach solution. For these experiments, the 212 Chamber sample was leached for 2 h at 150°C in the autoclave. The autoclave was cooled to 95-100°C, and the slurry was then filtered hot. The filtrate was transferred to a reaction vessel which was maintained at 95°C. Next, 250 mL samples of the hot solution were contacted with 10-g portions of three of the resins and with activated carbon, and the resin-solution slurries were held at ~95°C for 2 h prior to sampling to assess the extent of Sb adsorption. The results of these experiments are summarized in Table 32. The results suggest a minor amount of As extraction, but the differences in As concentration could be the consequence of minor, and undetected, changes in the volume of the samples during the 2-h equilibration period (compare the analyses for the "blank" test). Clearly, none of the ion exchange resins extracts any significant amount of Sb. In contrast, activated carbon seems to adsorb a minor amount of Sb, but unfortunately, the carbon co-sorbs a more significant amount of the associated arsenic. Of the reagents tested, however, only the activated carbon seems to offer any potential for Sb removal from the near-neutral As_2O_3-containing water leach solutions.

Table 32 - Extraction of Antimony From the Hot (95°C) Water Leach Solutions

Resin	Concentration of the Hot Solution Before the Addition of the Resin or Carbon As (g/L)	Sb (g/L)	Concentration of the Hot Solution After 2 h of Contact with the Resin or Carbon As (g/L)	Sb (g/L)
Blank	56.6	0.243	55.5	0.235
Gravex GR-2-0	56.6	0.243	55.4	0.231
Duolite C-467	56.8	0.237	55.9	0.231
Hycarb 6x12	56.8	0.237	52.7	0.168

The generally negative extraction results are probably related to the aqueous chemistry of antimony. If any cationic resin is to extract antimony, the element must be present as a cationic species. It is known that Sb(V) does not form water soluble cationic species. Although Sb(III) can form an antimonyl ion, SbO^+, the species exists only in acid media (6). Consequently, it is unlikely that antimony can be extracted with cationic exchange resins unless the pH of the solution is lowered. To pursue this option, the 212 Chamber sample was leached in hot water, the slurry was filtered and the filtrate was cooled to room temperature. One hundred millilitre aliquots of the solution were acidified to pH 3.0 or pH 1.0 with H_2SO_4. The acidified solutions were contacted with 2 mL of the various resins and agitated gently for 2 h prior to sampling. The results of these studies are given in Table 33, in which the Sb concentrations should be compared to the initial concentration of 0.0245 g/L Sb. Minimal Sb extraction occurs at pH 3.0, but a more significant level of extraction is observed at pH 1.0. In particular, the Duolite C-467 ion exchange resin extracted >90% of the Sb from the pH 1.0 solution. Although acidification coupled with ion exchange could likely be used to control antimony, the use of strongly acid media is not compatible with the simple hot water leaching option outlined in Figure 41.

Table 33 - Extraction of Antimony by Various Ion Exchange Resins at Room Temperature and pH 3.0 or pH 1.0

Resin	pH	Sb Concentration in Raffinate (g/L)	Total Sb Extracted (%)
Gravex GR-2-0	3.0	0.0246	0.0
Amberlite IRC-120	3.0	0.0238	0.2
Amberlite IRC-50	3.0	0.0232	2.1
Duolite C-467	3.0	0.0236	0.5
Gravex GR-2-0	1.0	0.0229	11.9
Amberlite IRC-120	1.0	0.0229	11.9
Amberlite IRC-50	1.0	0.0226	13.1
Duolite C-467	1.0	0.0022	91.7

Re-Sublimation of the As_2O_3-Rich Dusts

The underlying objective of this part of the study was to produce a marketable As_2O_3 product by the re-sublimation of the as-received As_2O_3-rich dusts. The index of success of the re-sublimation process is the purity of the re-sublimed As_2O_3, and to a lesser extent, the total percentage of arsenic sublimed. As will be seen, iron and the silicate minerals do not sublime, and as a result, Sb is the only impurity of any significance in the re-sublimed As_2O_3 product.

The effect of the re-sublimation temperature and the sublimation atmosphere (oxidizing, neutral or reducing) on the As/As+Sb percentage of the re-sublimed oxide product is illustrated in Table 34 and Figure 44. These data were generated for the 212 Chamber sample which analyzes 45.20% As and 2.13% Sb. It is apparent that the purity of the oxide depends directly on the temperature. As the re-sublimation temperature increases from 250°C to 550°C, the As/As+Sb percentage decreases from ~99.5% to 96-97%. Significantly, the Sb contents of the re-sublimed oxide are 0.15 - 0.66% Sb; accordingly, many of the re-sublimed products contain >0.2% Sb and might be difficult to market. All of the products made at temperatures greater than the boiling point of As_2O_3 (~350°C) had unacceptably high Sb contents. It also appears that the gaseous atmosphere affects the relative purity of the re-sublimed oxide, although there is some scatter of the data obtained. Oxidizing atmospheres, such as those produced using air or O_2 gas, seem to yield the highest purity products, and the products made under oxidizing conditions were consistently white. Neutral atmospheres (N_2 or He gases) and a reducing atmosphere (H_2 gas) seem to yield oxide products having similar purities. Although the products made using neutral atmospheres were also white, those generated under reducing conditions were consistently grey. Nevertheless, X-ray diffraction analysis showed all the re-sublimed oxide products to consist only of As_2O_3 having the cubic arsenolite structure. Based on the results presented above, the decision was made to carry out all subsequent re-sublimation tests using an air atmosphere.

The results presented above indicate that low sublimation temperatures yield higher purity oxide products. Accordingly, the re-sublimation reaction was monitored as a function of time at 259°C using the 212 Chamber sample, which analyzes 56.2% As and 2.13% Sb. Figure 45 illustrates the extent of reaction, reported as the percentage of the original sample mass remaining unsublimed, as a function of the heating time at 259°C. The sublimation takes place in a nearly linear manner for the first 5-6 h of heating, but subsequently, the reaction slows and eventually levels off after about 10 h of heating. Still longer heating times have no significant effect on the amount of sample sublimed. Ultimately, about 25% of the original mass of the sample remains in the residue at 259°C. Table 35 presents the compositional data of the various samples produced in the heating experiments outlined in Figure 45. In total, about 75% of the initial mass of the sample sublimes; however, 93% of the initially present arsenic sublimes under the same conditions. This reflects the significantly higher volatility of As_2O_3 relative to the silicate minerals and iron oxide impurities present in the sample. As will be shown later, the residual ~7% of the arsenic is present in the residue as poorly volatile $(Sb,As)_2O_3$ and iron arsenate ($Fe_2As_4O_{12}$) species. The compositional data indicate that the initially re-sublimed oxide has the highest purity and that the purity decreases with prolonged heating times. Likely, a heating time of 10-12 h would be required to re-sublime most of the arsenic present in the 212 Chamber sample at 259°C. For such heating periods, it appears that the re-sublimed oxide would contain ~99.6% As_2O_3 and ~0.4% Sb. Clearly, only the very initial products meet the stipulated antimony content of <0.2% Sb.

Table 34 - Influence of Temperature and the Type of Atmosphere on the Purity of the Re-sublimed Arsenic Oxide

Temperature (°C)	Oxidizing Atmosphere		Neutral Atmosphere		Reducing Atmosphere	
	As/As+Sb (%)	Sb (wt %)	As/As+Sb (%)	Sb (wt %)	As/As+Sb (%)	Sb (wt %)
299	99.46	0.16	99.47	0.39	-	-
	99.80	0.15	-	-	-	-
	99.78	0.39	-	-	-	-
	99.67	0.24	-	-	-	-
	99.10	0.66	-	-	-	-
272	-	-	99.47	0.41	-	-
386	-	-	97.61	1.82	-	-
400	-	-	97.50	1.85	-	-
450	-	-	97.18	2.18	-	-
459	98.35	1.41	-	-	-	-
472	-	-	-	-	96.27	2.91
475	-	-	97.54	1.89	-	-
513	-	-	-	-	97.00	2.31
519	-	-	96.97	2.33	-	-
545	98.67	0.96	-	-	-	-

Table 35 - Effect of Heating Time at 259°C on the Percentage of the Total Arsenic Sublimed From the 212 Chamber Sample, and the Purity of the Re-sublimed Product

Heating Time (h)	Residue Mass (% of Initial)	As Sublimed (% of Initial)	Product Composition	
			As_2O_3 (%)	Sb (%)
0	100	0	–	–
2	79.5	32.1	99.80	0.15
4	60.1	–	–	–
6	44.5	69.9	99.71	0.21
8	32.6	–	–	–
10	29.2	–	–	–
12	28.2	91.9	99.57	0.31
20	27.8	93.3	99.46	0.39
30	27.0	–	–	–

Although most of the re-sublimation studies were done using the 212 Chamber sample, a direct comparison of the thermal behaviour of all four As_2O_3-rich dusts was made. For these comparative tests, samples of each dust were heated at 545°C for 10 h in static air. The sublimates were collected and analyzed; the results are summarized in Table 36. In all instances, the re-sublimation process yields a relatively pure oxide product, which consistently has a higher As/As+Sb percentage relative to that of the starting material. In fact, Figure 46 suggests that there is a nearly linear relationship between the percentage of As/As+Sb in the re-sublimed product and As/As+Sb percentage of the original As_2O_3-rich dust. This behaviour implies that antimony in all the As_2O_3-rich dusts behaves in a similar manner during thermal processing. Accordingly, the trend identified in Figure 46 might be useful for predicting the re-sublimation response of other dust samples. The re-sublimation procedure reduces the Sb content of the As_2O_3 product, but aside from the 236 Chamber sample, all the re-sublimed products have Sb contents greater than the specified 0.2% Sb limit. The Au analyses also presented in Table 36 demonstrate that gold collects almost quantitatively in the re-sublimation residues. As a consequence, all of the re-sublimed oxide products contained <0.03 ppm Au, the detection limit of the analytical procedure used.

Table 36 - Purities of the Re-sublimed As_2O_3 Products Made When the Four As_2O_3-rich Dusts were Heated to 545°C for 10 h in Static Air

Sample	As/As+Sb in Sample (%)	As/As+Sb in Product (%)	As in Product (%)	Sb in Product (%)	Au in Sublimation Residue (ppm)
January 98 Composite	98.74	99.57	72.3	0.31	16.82
April 97 Composite	97.83	98.90	70.4	0.78	28.84
212 Chamber	96.35	98.67	71.4	0.96	42.90
236 Chamber	99.49	99.94	71.7	0.04	26.64

The results presented above indicate a modest level of Sb_2O_3 re-sublimation along with that of As_2O_3, despite a significant difference in the vapour pressures of the two end-member oxides. The limited mass spectrographic work carried out in support of the project helps to explain the unexpected transport of Sb_2O_3 along with As_2O_3. It is known that both As_2O_3 and Sb_2O_3 exist as polymerized species in the vapour state; i.e., in fact, the vapour species are predominantly As_4O_6 and Sb_4O_6 (3). The mass spectrographic analysis of the sublimed vapour from the 212 Chamber sample detected the presence of mixed As-Sb oxide species, notably, As_3SbO_6. Such mixed As-Sb oxide species presumably have a vapour pressure lower than that of end-member As_2O_3, but significantly higher than that of end-member Sb_2O_3. The result is the significant transport of Sb_2O_3 at temperatures much lower than those needed to vapourize end-member Sb_2O_3. As a result, the re-sublimed As_2O_3 has a significant Sb content although the As/As+Sb percentage of the sublimate is consistently higher than that of the starting As_2O_3-rich dust.

In an effort to eliminate Sb from the mixed vapour species, such as As_3SbO_6, the As_2O_3-rich dust was mixed with metallic arsenic and was re-sublimed in a flowing H_2 gas stream. The intent was to minimize the amount of Sb transported by utilizing the following reaction.

$$As_3SbO_6 + As \div As_4O_6 + Sb \qquad (7)$$

To investigate this option, 2.21 g of 99.99% As metal powder was mixed with 8.78 g of the 212 Chamber dust, and the mixture was heated for 16 h at 545°C. A hydrogen atmosphere was employed to prevent the possible oxidation of the elemental arsenic. The presence of the arsenic metal increases the As_2O_3 content of re-sublimation product, but only to a limited extent. With the arsenic metal present in the system, the re-sublimed product contained 98% As_2O_3; in the absence of the arsenic metal the product consisted of 97% As_2O_3. Although the presence of arsenic metal improves the quality of the re-sublimed As_2O_3 product, the improvement is not likely great enough to justify the pursuit of this option.

Mineralogical Investigations of the Sublimation Residues

Mineralogical studies were carried out on the residues produced by heating the January 98 Composite, the April 97 Composite and the 236 Chamber samples for 10 h at 545°C in static air, and the 212 Chamber sample for 20 h at 610°C in static air.

X-ray diffraction analyses of the four sublimation residues were carried; the individual diffraction patterns are presented in Appendix 8, and it should be noted that all of the sublimation residues appear to contain a significant amount of amorphous material. The sublimation residue from the January 98 Composite sample consists of an As_2O_3-type compound, iron arsenate ($Fe_2As_4O_{12}$), anhydrite ($CaSO_4$) and quartz. The corresponding residue from the heating of the April 97 Composite sample consists of an As_2O_3-type compound, iron arsenate ($Fe_2As_4O_{12}$), anhydrite ($CaSO_4$), quartz and muscovite. A trace amount of As metal was also detected in this sample, but the presence of elemental arsenic requires independent confirmation. The sublimation residue from the heating of the 236 Chamber sample was shown to contain abundant muscovite, chlorite, quartz and iron oxide (Fe_2O_3), in addition to the As_2O_3-type compound, iron arsenate ($Fe_2As_4O_{12}$) and anhydrite ($CaSO_4$). A trace amount of $Fe_8(AsO_4)_6(OH)_6.5H_2O$ may also be present, but the occurrence of this hydrous phase requires confirmation. The sublimation residue from the heating of the 212 Chamber sample was shown by X-ray diffraction analysis to consist of hematite, maghemite (Fe_2O_3), anhydrite ($CaSO_4$), chlorite, muscovite, K-feldspar and quartz. Significantly, the As_2O_3-type compound and iron arsenate ($Fe_2As_4O_{10}$) were not detected in this sublimation residue by X-ray diffraction analysis. Their absence could be a consequence of the somewhat higher temperature (610°C versus 545°C) and longer heating time (20 h versus 10 h) used to generate this material.

Figure 47 shows the general appearance of the sublimation residue from the January 98 Composite sample. The residue clearly has sintered into 100-500 µm aggregates which have irregular outlines. The brighter masses are rich in As, but also contain minor amounts of O, as well as traces of Sb and Fe. This phase is presumably $(As,Sb)_2O_3$, although the presence of finely dispersed As metal cannot be precluded. The darker appearing masses are mostly silicates, iron arsenate and iron oxide; one such occurrence is shown in more detail in Figure 48. The sintered agglomerate contains bright appearing particles of iron arsenate (presumably $Fe_2As_4O_{12}$), as well as darker appearing grains of $CaSO_4$, muscovite and quartz. The various particles clearly have sintered together, but there is not an obvious agglomerating phase in this image. In some instances, however, the particles may be sintered by $(Sb,As)_2O_3$. Overall, the SEM-EDX studies of this sublimation residue showed it to consist of major iron arsenate ($Fe_2As_4O_{12}$ or $FeAs_2O_3$ having a minor Sb content), $CaSO_4$, muscovite and quartz. The iron arsenate phase commonly contains trace amounts of Ca, K, S, Si and Al, but some of the impurities detected may originate from dispersed silicate grains. Minor amounts of As_2O_3, containing traces of Sb, are present along with trace amounts of elemental As. Isolated particles of calcium arsenate having a minor Fe and trace S content were detected, and a few grains of Na-Al silicate were evident.

The SEM-EDX study of the sublimation residue from the heating of the April 97 Composite sample showed this material to be similar to the residue from the January 98 Composite sample. Figure 49 shows the detailed texture of the sublimation residue from the April 97 Composite sample. This material consists of bright grains of iron arsenate ($Fe_2As_4O_{12}$ or $FeAs_2O_3$) having a minor Sb content. The abundance of the iron arsenate species reflects their significant stability at elevated temperatures. A few particles are rich in Sb, As and Fe, and may be iron arsenate-antimonate compounds. Most of the grey appearing particles in

Figure 49 are muscovite, whereas the dark grains are $CaSO_4$ or quartz. Other species detected in trace amounts include As-bearing iron oxide and elemental arsenic. Minor amounts of As_2O_3 having a low Sb content were also detected, and as shown in Figure 50, the As_2O_3 phase tends to occur as large masses enveloping smaller particles of iron arsenate, muscovite and quartz.

The 236 Chamber sample contains less As_2O_3 but more silicate and oxide species than the January 98 Composite and April 97 Composite samples. As a result, the sublimation residue from the heating of the 236 Chamber sample contains more abundant oxide and silicate species. Figure 51 illustrates a number of iron arsenate ($Fe_2As_4O_{12}$) particles which are associated with needle-like grains of As_2O_3 containing minor amounts of Fe. Particles of $CaSO_4$, about 10 µm in size and having a modest As content, and dark appearing fragments of quartz are also evident. Most of the grey appearing grains are chlorite or muscovite. Other species detected in this sample include As-bearing iron oxide, calcium arsenate having a minor Fe content, and possibly, elemental arsenic.

Of the resublimed samples, the 212 Chamber sample was heated to be highest temperature and for the longest time. Despite this fact, the sublimation residue from the heating of the 212 Chamber dust still contained a few large fragments of arsenic oxide. One such fragment is illustrated in Figure 52 which shows a ~500 μm mass of arsenic oxide agglomerating various silicate and iron arsenate particles. EDX analysis showed the arsenic oxide to contain minor amounts of O, but only traces of Sb. The reasons for the persistence of large arsenic oxide masses at temperatures well above the sublimation temperature of As_2O_3 (465°C) are not clear. It may be that the oxide has a reduced O content and, consequently, a lower vapour pressure than stoichiometric As_2O_3. Alternatively, it is possible that the large masses form during the removal of the sample from the furnace, although the morphology does not convincingly support such a mechanism. Figure 53 shows a number of the finer grain constituents of the sublimation residue from the 212 Chamber sample in greater detail. The bright appearing grains are either iron oxide or iron arsenate. In this regard, both $Fe_2As_4O_{12}$ and $Fe_2As_4O_{12}$ containing trace Sb were detected. A few tiny bright grains of $(Sb,As)_2O_3$ were also evident, but this phase is surprisingly rare given the abundance of Sb in the 212 Chamber sample. Figure 53 illustrates some particles of Ca arsenate having a modest Fe content and of $CaSO_4$. Most of the dark appearing particles are chlorite, muscovite or quartz. Figure 54 provides a different view of the same sublimation residue. In addition to the phases identified above, the figure illustrates several particles of $CaSO_4$ and quartz. The fine grained residues presented in Figures 53 and 54 illustrate the non-volatile phases which are concentrated when the arsenic-antimony oxide species are sublimed.

Arsenic Solubility in Acid Media

The intent of these scoping experiments was to evaluate the possibility of enhancing the solubility of As_2O_3 from the As_2O_3-rich dusts by the use of an acid medium in place of water. All of the acid leaching tests were based on the use of the 236 Chamber sample which contains 58.0% As and 0.30% Sb (see Table 2). This sample has the lowest Sb content of any of the four dusts studied, and accordingly, the results obtained likely should be validated for the more Sb-rich samples.

The initial series of experiments was intended to clarify the effect of the concentration of HNO_3 on the solubility of As_2O_3 over the 236 Chamber sample. Figure 55 shows the solubility curves realized when 125 g/L of the 236 Chamber sample was slurried at 95°C in the presence of 1.0, 2.0, 3.0 and 4.0 M HNO_3. In all instances, the As_2O_3 dissolves rapidly and a near-steady state concentration is noted within ~30 min. Comparison with Figures 34 and 35 suggests that the As_2O_3 dissolves more rapidly in acid media than in water, and this effect could be attributable to the dissolution of the inhibiting Sb content of the As_2O_3 crystals in an acid solution. Another interesting feature is that the solubility seems to decrease with increasing HNO_3 concentration, for concentrations >1.0 M HNO_3. The reasons for this behaviour are not clear, but may be related to the use of HNO_3. Similar behaviour does not seem to occur for hydrochloric acid solutions, although more work would be needed to substantiate this conclusion.

The solubilities of Sb and Fe were also monitored during the experiments, and the data obtained in the 2.0 M HNO_3 solution are presented in Figure 56. The detailed solubility data for As, Sb and Fe for all the experiments are presented in Appendix 9, from which it is clear that the concentration of HNO_3 has little influence on the solubility of Sb and Fe from the 236 Chamber sample. In all cases, the dissolution of Sb increases for the first ~10 min of reaction, but remains relatively constant for the remainder of the 2-h experiment. The Sb concentrations are relatively low (<150 mg/L Sb) and exhibit some scatter. The Fe concentrations are relatively high and increase progressively with time during the solubility experiment. High concentrations of Sb and Fe are characteristic of the use of acid media. The great advantage of the water leaching system is its selectivity for As_2O_3. Any acid-based leaching system would have to incorporate Sb and Fe removal circuits. As shown in Table 33, ion exchange resins can remove Sb from acidic media, and a number of options are available for Fe control from acid solutions (7).

Following the 2-h leaching experiment, the slurry was filtered hot, and the clear solution was cooled to room temperature to crystallize As_2O_3. Table 37 summarizes the amount of As_2O_3 precipitated in each experiment, as well as the composition of the As_2O_3 crystals. Approximately 20 g of As_2O_3 precipitates, and there is not a clear relationship between the amount of As_2O_3 precipitated and the As_2O_3 solubility in the different HNO_3 media. This may reflect the need to control the cooling-crystallization procedure more closely. In any event, the use of any HNO_3 concentration yields significantly more As_2O_3 product than does water leaching (0.0 M HNO_3) for 2 h at 95°C. Of course, the proposed hot water leach procedure, wherein the dust is leached for 2 h at 150°C followed by cooling to 95°C, filtration, and subsequent cooling to 25°C (Figure 41), yields significantly more As_2O_3 product than any of these acid leaching tests. The hot water leach procedure, as applied to the 236 Chamber sample, yielded 45-50 g of As_2O_3 product. All of the As_2O_3 products precipitated from nitric acid media contain detectable amounts of Sb and Fe that reflect the presence of these impurities in the leach solutions. The high Sb content of the As_2O_3 products made from the 0.0 M and 4.0 M HNO_3 solutions is likely a consequence of the lower masses of product generated from these solutions. Nevertheless, it appears possible to produce an As_2O_3 product containing ~ 0.04 % Sb and ~ 0.004 % Fe, and the impurity contents are lower than those noted in the water leaching experiments (cf. Table 27).

Table 37 - Amount and Composition of the As_2O_3 Products Formed on Cooling the Solutions from the Nitric Acid Leaching of the 236 Chamber Sample

HNO_3 (mol/L)	Mass As_2O_3 (g)	% As	% Sb	% Fe
0.0	8.0	76.1	0.17	0.011
1.0	21.7	76.2	0.02	0.002
2.0	26.6	77.3	0.02	0.003
3.0	24.3	77.9	0.04	0.004
4.0	16.8	77.9	0.10	0.002

As shown by the X-ray diffraction patterns given in Appendix 10, the acid leach residues consist of major amounts of As_2O_3, together with muscovite, quartz and chlorite. For the short reaction times and acid concentrations used, there is minimal acid dissolution of the silicate minerals. The high As_2O_3 content reflects the incomplete dissolution of As_2O_3 for the high initial pulp density (125 g/L) used. X-ray diffraction analysis of the As_2O_3 products formed on cooling the acid leach solutions detected only As_2O_3 having the cubic arsenolite structure. The X-ray diffraction patterns of the various As_2O_3 products are also given in Appendix 10.

Following crystallization and filtration of the As_2O_3 product, the clarified solution was neutralized to pH 9.0 with solid Na_2CO_2 to try to precipitate additional As_2O_3. As shown in Table 38, however, this procedure was largely unsuccessful. Only a few grams of precipitate formed despite the very large amount of Na_2CO_3 added. Further, the composition is not that of As_2O_3. The neutralization precipitates were difficult to filter, and the poor filtration properties may reflect the abundance of iron oxy-hydroxide compounds. X-ray diffraction analyses of the neutralization precipitates were carried out, and the various X-ray diffraction patterns are given in Appendix 10. They show the neutralization precipitates to be nearly amorphous. The few distinct diffraction lines present correspond to $NaNO_3$, the product of the neutralization of nitric acid with Na_2CO_3. Washing of the neutralization precipitates was not carried out in order to avoid the dissolution of any additional As_2O_3 which may have precipitated.

Table 38 - Amount and Composition of the Precipitates Formed by Neutralizing the Nitric Acid Leach Solution to pH 9.0

HNO_3 (mol/L)	Na_2CO_3 used (g)	Mass Precipitate (g)	As (%)	Sb (%)	Fe (%)

1.0	76	2.1	25.8	0.81	5.4
2.0	125	3.2	28.2	1.09	6.4
3.0	170	2.9	25.7	1.05	6.7
4.0	226	4.1	29.2	0.83	6.7

The effect of the concentration of HCl and H_2SO_4 on the amount of As_2O_3 product formed was also ascertained. These experiments involved leaching 125 g/L of the 236 Chamber sample for 2 h at 95°C in solutions having various concentrations of HCl or H_2SO_4. The leach slurries were filtered hot, and the clear solutions were then cooled to 25°C to crystallize As_2O_3. The As_2O_3 product was filtered, dried and weighed. As the data presented in Table 39 indicate, the use of either HCl or H_2SO_4 generates more As_2O_3 product than does simple water leaching for 2 h at 95°C. It appears that increasing the H_2SO_4 concentration from 1.0 M to 2.0 M H_2SO_4 results in a reduction in the amount of As_2O_3 product formed. A similar trend was identified for the effect of the concentration of HNO_3 on the product yield, but more closely controlled cooling-crystallization conditions would be needed to substantiate these findings. In contrast, increasing concentrations of HCl actually increase the amount of As_2O_3 formed, although the increase is only ~10%. Significantly, the 45 g of As_2O_3 product, obtained under non-optimized conditions, is similar to the amount generated by the hot water leach procedure (45-50 g As_2O_3). In this respect, HCl leaching of the dust appears attractive, but the method would have to be verified for an Sb-rich dust sample.

Table 39 - Amount of As_2O_3 Product Formed on Cooling the Solutions from the Leaching of the 236 Chamber Sample in Various Concentrations of Sulphuric Acid or Hydrochloric Acid

Acid	Concentration (mol/L)	Mass As_2O_3 (g)
Water	-	8.0
H_2SO_4	1.0	32.5
H_2SO_4	2.0	25.2
HCl	0.75	41.9
HCl	2.0	40.1
HCl	3.0	45.4

The effect of the initial pulp density on the amount and composition of the As_2O_3 product was investigated using 2.0 M HNO_3 media at 95°C. Figure 57 shows the As_2O_3 leaching curves generated for initial pulp densities of 75, 125 and 175 g/L of the 236 Chamber dust. Within the errors involved, all the leaching curves are similar. The implication is that sufficient dust must be added to produce a "saturated" solution and that further increases in the amount of solids have little effect on the As_2O_3 solubility. For the dust sample used, an initial pulp density of 75 g/L is slightly more than that required for As_2O_3 saturation. This point is further illustrated by the X-ray diffraction patterns of the three leach residues that are given in Appendix 10. All the patterns show the presence of muscovite, chlorite and quartz. The pattern for the residue from the 75 g/L solids experiment contains only a minor amount of As_2O_3, whereas the residue from the 125 g/L solids test contains a major amount of As_2O_3.
The X-ray diffraction study of the residue from the 175 g/L solids experiment detected a dominant amount of As_2O_3, and correspondingly minor quantities of the silicate species.

The detailed analytical data for all the pulp density experiments are presented in Appendix 9. The results show that the dissolution of Sb is essentially the same at all the pulp densities studied. In this regard, Sb behaves very similarly to As. In contrast, the Fe concentration clearly increases with increasing pulp density, and this trend is more clearly illustrated in Figure 58. The dissolved iron concentration increases systematically with time at any pulp density. For a given leaching time, the amount of dissolved iron increases with increasing initial pulp density. Presumably, the dissolved iron originates from the leaching of iron oxide and iron arsenate species. Hence, the dissolution behaviour of Fe in acid media is largely independent of that of As, and because $Fe(NO_3)_3$, $FeCl_3$ and $Fe_2(SO_4)_3$ have high solubilities in acid solutions, the iron solubility can increase even after the solution is "saturated" with As_2O_3.

As expected from the similar As_2O_3 solubilities realized at the different initial pulp densities (Figure 57), similar amounts of As_2O_3 product were formed on cooling the filtrates to room temperature. Table 40 presents the mass of As_2O_3 product recovered at each pulp density, as well as the composition of the product. About 28 g of As_2O_3 was collected in each experiment; the minor differences in mass presumably reflect the need to improve and standardize the cooling-crystallization procedure. All the As_2O_3 products contain low levels of Sb and Fe, and it seems that the Sb content decreases as the pulp density increases.

Table 40 - Effect of the Initial Pulp Density on the Amount and Composition of the As_2O_3 Product from the Leaching of the 236 Chamber Sample in 2.0 M HNO_3 at 95°C

Pulp Density (g/L)	Mass As_2O_3 (g)	As (%)	Sb (%)	Fe (%)
75	31.7	77.4	0.26	0.006
125	26.6	77.3	0.02	0.003
175	28.7	77.5	0.02	0.017

Neutralization of the solution from the As_2O_3 crystallization operation to pH 9.0 with Na_2CO_3 generated <3 g of a gelatinous precipitate. X-ray diffraction analysis (Appendix 10) showed the precipitate to be amorphous and to contain a minor amount of $NaNO_3$ which results from the neutralization of the nitric acid with Na_2CO_3. The crystalline phase shown on the diffraction patterns was identified as $CaCO_3$ by the computer search program, but $NaNO_3$ and $CaCO_3$ have virtually identical X-ray diffraction patterns.

The effect of temperature on the leaching of the 236 Chamber dust in 2.0 M HNO_3 was investigated using an initial pulp density of 125 g/L solids. Figure 59 presents the As_2O_3 leaching curves realized at 55, 75 and 95°C; the detailed leaching data are presented in Appendix 9. Regardless of the leaching temperature, the As_2O_3 dissolves rapidly, such that near-steady state solubilities are realized within ~30 min. This is in contrast to the data obtained for the leaching of the As_2O_3-rich dusts in water (Figure 34) where several hours seem necessary to achieve a steady state solubility. As expected, the solubility of the As_2O_3-rich dust in 2.0 M HNO_3 media increases systematically with temperature; the solubility at 95°C is about twice that measured at 55°C.

X-ray diffraction analyses of the residues from the leaching tests done at the various temperatures were carried out, and the X-ray diffraction patterns are presented in Appendix 10. All of the patterns show the presence of muscovite, chlorite, quartz and As_2O_3 having the cubic arsenolite structure. The amount of As_2O_3 in the leach residue, however, increases significantly as the temperature is reduced. The residue from the leaching experiment done at 55°C shows a dominant amount of As_2O_3 that is consistent with the limited extent of As_2O_3 dissolution measured at that temperature (Figure 59).

Following the 2-h leaching period at each reaction temperature, the leach slurry was filtered hot and the clear filtrate was cooled to room temperature to crystallize As_2O_3. The amount of As_2O_3 product formed increases substantially as the temperature increases, as is shown in Table 41. Almost no precipitate was generated from the test done at 55°C, and the results in general suggest the advantages of carrying out the acid leaching experiments at as high a temperature as possible. Although the X-ray diffraction patterns of the precipitates (Appendix 10) indicate only the cubic arsenolite form of As_2O_3, the analytical data of Table 41 show the presence of small amounts of Sb and Fe. Significantly, the Sb and Fe impurity contents decrease as the temperature increases and the amount of product consequentially increases; this is an additional reason for carrying out the acid leaching experiments at an elevated temperature.

Table 41 - Effect of the Leaching Temperature on the Amount and Composition of the Product from the Leaching 125 g/L of the 236 Chamber Sample in 2.0 M HNO_3 at Various Temperatures

Temperature (°C)	Mass As_2O_3 (g)	As (%)	Sb (%)	Fe (%)
55	0.8	76.9	0.71	0.008
75	13.0	77.5	0.15	0.007
95	26.6	77.5	0.02	0.003

Following the crystallization of the As_2O_3 product, the slurry was filtered and the clear filtrate was neutralized to pH 9.0 with solid Na_2CO_3. The neutralization generated <3 g of a gelatinous precipitate which filtered poorly. X-ray diffraction analysis of these precipitates showed the presence of an amorphous phase, As_2O_3 and $NaNO_3$, which is incorrectly identified as calcium carbonate by the computer search program. As noted above, however, $NaNO_3$ and $CaCO_3$ have virtually identical X-ray diffraction patterns and the chemistry of the system suggests that $NaNO_3$ is the more likely species. The amorphous phase is believed to be the actual neutralization product. The As_2O_3 phase, which is especially evident in the lower temperature leaching experiments, could reflect the supersaturation of As_2O_3 in the low temperature leaching media, or possibly, a slightly enhanced level of As_2O_3 precipitation arising from the pH change.

Finally, an effort was made to compare the relative efficiency of nitric acid, hydrochloric acid and sulphuric acid for the leaching of As_2O_3 from the As_2O_3-rich dust. For these experiments, 125 g/L of the 236 Chamber sample was slurried in 1 L of 2.0 M HNO_3, 2.0 M HCl or 1.0 M H_2SO_4 media for 2 h at 95°C.

Figures 60, 61 and 62 present the As_2O_3 leaching curves realized using the three different acids, and the detailed leaching data are presented in Appendix 9. In all instances, As_2O_3 dissolves rapidly in the acid media, and nearly saturated solutions are achieved within 30 min at 95°C. Longer leaching times appear to have little additional effect on the solubility of As_2O_3, although tests extending for tens of hours would be required to validate this conclusion. Figure 63 compares the three leaching curves directly. It is apparent that the 2.0 M HNO_3, 2.0 M HCl and 1.0 M H_2SO_4 solutions yield similar solubilities. Figures 64 and 65 compare the analogous Sb and Fe solubilities from the 236 Chamber sample in the three acids. In all instances, there is an enhanced solubility of Sb and Fe relative to that measured in water. It is tentatively postulated, in fact, that the enhanced solubility of As_2O_3 is due to the dissolution of antimony which otherwise would "passivate" the As_2O_3-rich dust to dissolution in water at temperatures <100°C. Hydrochloric acid solutions seem to be the most effective media for the dissolution of Sb. It has been demonstrated previously (5,8) that Sb_2O_3 is readily soluble in HCl media, although the solubility is not as high as that in NaOH media, where sodium antimonate species are formed. In contrast, As_2O_3 is less soluble in both HNO_3 and H_2SO_4 media (6). It seems that the dissolution of the minor Sb content of the dust allows the major As_2O_3 component to leach freely, but the detailed mechanisms involved are not known. All the acid solutions, and especially the 2.0 M HCl medium, result in the dissolution of a significant amount of iron, and the extent of iron dissolution increases throughout the 2-h leaching experiments. The enhanced level of iron dissolution relative to that measured in the water leaching experiments is undesirable and would necessitate the installation of an iron removal circuit (7) in any acid-based leaching process.

X-ray diffraction analyses of the residues from the leaching of the 236 Chamber sample in the different acids at 95°C were carried out. The X-ray diffraction patterns and computer-derived phase identifications are given in Appendix 10. The three residues are similar, and contain muscovite, chlorite and quartz. A major amount of As_2O_3 having the cubic arsenolite structure also is detected. Its presence reflects the fact that the initial 125 g/L solids pulp density used for the experiments provides an excess of As_2O_3 for the leaching reaction; the excess As_2O_3 remains in the leach residue. In an optimized acid leaching process, the initial pulp density would be adjusted to minimize the amount of As_2O_3 remaining in the leach residue.

The slurries from the leaching of the 236 Chamber sample in 2.0 M HNO_3, 2.0 M HCl and 1.0 M H_2SO_4 media were filtered at the 95°C leaching temperature. The clear filtrates were cooled to room temperature to crystallize an As_2O_3 product. As Table 42 indicates, about 30 g of As_2O_3 crystallized from the 2.0 M HNO_3 and 1.0 M H_2SO_3 solutions; however, more than 40 g of product, formed on cooling the 2.0 M HCl solution. The Sb and Fe contents of the crystallized As_2O_3 product are also given in the table. Hydrochloric acid media dissolve more Sb than nitric or sulphuric acid media (Figure 64). This enhanced solubility is reflected in the modest Sb content of the As_2O_3 product made from the HCl solution. Likely, therefore, a hot ion exchange step would be required for Sb control in an HCl-based process. Despite the elevated Fe concentration of the HCl leaching medium, the resulting As_2O_3 product has a low Fe content. This implies that an acid leaching process would be relatively insensitive to modest concentrations of dissolved iron and that only a small bleed of solution for iron control would be required.

Table 42 - Amount and Composition of the As_2O_3 Products Crystallized from the Solutions Containing 2.0 M HNO_3, 2.0 M HCl or 1.0 M H_2SO_4

Acid	Mass As_2O_3 (g)	As (%)	Sb (%)	Fe (%)
2.0 M HNO_3	26.6	77.5	0.02	0.003
2.0 M HCl	40.1	78.5	0.13	0.004
1.0 M H_2SO_4	32.5	77.5	0.06	0.005

X-ray diffraction analyses of all the products detected only the cubic arsenolite form of As_2O_3, and the various X-ray diffraction patterns are given in Appendix 10.

Following filtration of the As_2O_3 crystal products, the clear filtrates were neutralized to pH 9.0 in an effort to precipitate additional amounts of As_2O_3. As Table 43 indicates, however, only a few grams of precipitate formed in any of the experiments. In all cases, the precipitates were gelatinous and difficult to filter; they were not water washed to avoid the dissolution of any As_2O_3 which may have formed. Only 2-3 g of precipitate formed on neutralization of the 2.0 M HNO_3 or 1.0 M H_2SO_4 solutions. About 8 g of product formed during the neutralization of the 2.0 M HCl solution, but the low As content of the precipitate indicates that As_2O_3 is not the major compound precipitated. All the precipitates contain a significant amount of iron, and the elevated iron tenor is not unexpected given the relatively large amount of iron dissolved in all the acid leaching experiments. The high iron content of the residue from the neutralization of the 2.0 M HCl solution suggests that much of the precipitate is an amorphous iron oxy-hydroxide phase.

Table 43 - Amount and Composition of the Precipitates Formed on Neutralization of the 2.0 M HNO_3, 2.0 M HCl and 1.0 M H_2SO_4 Solutions to pH 9.0 With Na_2CO_3

Acid	Mass Precipitate (g)	As (%)	Sb (%)	Fe (%)
2.0 M HNO_3	3.2	28.2	1.09	6.4
2.0 M HCl	8.2	27.5	1.46	6.2
1.0 M H_2SO_4	2.2	23.7	0.24	3.3

X-ray diffraction analyses of the precipitates formed on neutralization of the acid solutions to pH 9.0 with solid Na_2CO_3 were carried out, and the resulting X-ray diffraction patterns are presented in Appendix 10. The residue from the neutralization of the 2.0 M HNO_3 solution is mostly amorphous but contains some crystalline $NaNO_3$. The sodium nitrate is the neutralization product of the HNO_3 with Na_2CO_3 that is present because the neutralization precipitate was not water washed in order to avoid the dissolution of any As_2O_3 which may have formed. The residue from the neutralization of the 2.0 M HCl solution is amorphous but contains some crystalline NaCl. The sodium chloride is the product of the neutralization of HCl with Na_2CO_3, and is detected because the neutralization precipitate was not water washed. The residue from the neutralization of the 1.0 M H_2SO_4 with Na_2CO_3 appears to be amorphous. None of the residues from the neutralization of the various solutions contains major amounts of crystalline As_2O_3. This fact, coupled with the small amounts and low purities of the residues, implies that the neutralization of the acid leach liquors is not a promising avenue for further research. This conclusion is also supported by the expected high reagent costs (acid plus neutralizing agent) which would be associated with the neutralization option.

Acid leaching of the As_2O_3-rich dusts offers advantages over water leaching with respect to dissolution rates and solubility limits. A schematic flowsheet, based on HCl leaching, is presented in Figure 66, and similar flowsheets could be developed for either nitric or sulphuric acid leaching media. In this option, the As_2O_3-rich dust would be contacted with a hydrochloric acid leaching solution at ~100°C and at atmospheric pressure. The initial pulp density (g/L solids) would be optimized to give a high dissolved As_2O_3 concentration and a low As_2O_3 content in the leach residue. Although a 2-h retention time is proposed, it seems likely, based on the initial test work, that the retention time could be reduced to <1 h. The leach slurry would be filtered hot, and the residue, which would constitute about 15% of the initial mass and would always contain some As and Sb, would be processed in a stabilization circuit. The hot, clear filtrate would next be treated by ion exchange for Sb removal. Next, the solution would be cooled to room temperature to crystallize an As_2O_3 product. The As_2O_3 would be filtered and washed with a small quantity of cold water prior to drying and packaging. The clear solution, which would contain ~2.0 M HCl, would be recycled to the leaching stage without neutralization. It would be necessary, however, to bleed a small amount of this solution to control iron, which also dissolves in the acid leaching circuit. The dissolved iron could be eliminated by aeration-neutralization or by solvent extraction methods (7). The size of the bleed stream likely would be dictated by the Fe content of the As_2O_3 crystals, but initial indications (Table 47) are that the bleed stream would be small. Although this flowsheet is more complex than that of the proposed hot water leaching procedure (Figure 41), it has the advantage that a high temperature autoclave is not required.

CONCLUSIONS

Four samples of As_2O_3-rich dust from the Giant Mine were supplied by Royal Oak Mines Inc. Two of the dust samples were recent composites, and were identified as the January 98 Composite and the April 97 Composite. These samples analyzed in excess of 87% As_2O_3, and contained ~1% Sb, as well as minor amounts of Fe, Al, Ca, Mg and Si. The two remaining samples were taken from the underground storage chambers; they were identified as the 212 Chamber and 236 Chamber. The latter samples contained only ~75% As_2O_3, as well as minor amounts of Fe, Al, Ca, Mg and Si. The 212 Chamber sample had an Sb content of 2.13%, whereas the 236 Chamber sample assayed only 0.30% Sb. The gold content of the As_2O_3-rich dusts varied from 2-11 ppm Au.

Mineralogical study of the four As_2O_3-rich dust samples, using X-ray diffraction analysis, scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and quantitative electron microprobe analysis, showed the four samples to be similar. With only a few minor exceptions, the same species are present in the four samples, and in approximately the same amounts. These species are tabulated in a qualitative manner below.

Species	January 98 Composite	April 97 Composite	212 Chamber	236 Chamber
As_2O_3	major	major	major	major
Fe arsenate	minor	minor	minor	minor
$(Sb,As)_2O_3$	minor	minor	minor	trace
Ca-Fe arsenate	trace	trace	minor	trace
Fe arsenate-sulphate	trace	trace	trace	very rare
Iron oxide	trace	trace	trace	trace
Ca-Fe oxide	very rare	trace	trace	very rare
Ca sulphate	very rare	very rare	trace	very rare
Chlorite	minor	minor	minor	minor

Quartz	trace	trace	trace	trace
Muscovite	minor	minor	minor	minor

The two more recent samples, the January 98 Composite and the April 97 Composite, have similarly high As_2O_3 contents, and contain relatively small amounts of impurity oxide or silicate phases. The two older samples from the underground storage caverns, the 212 Chamber and the 236 Chamber, have less As_2O_3 but relatively high silicate contents that likely reflect non-optimal operation of the roasting circuit in the past. The Sb contents of the dusts vary from 0.30 to 2.13% Sb, and this variation affects the solid solution Sb content of the As_2O_3 crystals, as well as the amount and composition of the minor $(Sb,As)_2O_3$ phase. In all cases, the dominant arsenic carrier is Sb-bearing As_2O_3, which normally occurs as tiny euhedral crystals, but sometimes is present as large irregular masses. A minor amount of the arsenic is present as an As-bearing iron oxide and as an iron arsenate phase, in which the arsenic content varies from 1.9 to 38% As. A Ca arsenate phase and Ca-Fe arsenate phase are only minor As carriers in any of the dust samples studied. Most of the Sb in the As_2O_3-rich dust samples is present in solid solution in the As_2O_3 crystals. The Sb content of the As_2O_3 varies from 0 to 47%. The more Sb-rich compositions are actually a $(Sb,As)_2O_3$ phase. A minor amount of the total Sb substitutes for As in the iron arsenate phase, and traces of Sb occur in the Ca arsenate, Ca-Fe arsenate and Fe arsenate-sulphate phases. Unlike As and Sb, the majority of the iron occurs in silicate form or as As-bearing iron oxide. Lesser amounts of the total iron are present as iron arsenate or Ca-Fe arsenate containing 5-10% Fe. The principal silicate species are chlorite (chamosite?), muscovite and quartz; however, trace quantities of Mg silicate, Fe-Ca-Al silicate-sulphate, K-Mg-Al silicate, Na-Mg-Al silicate, Ca-Na-Mg-Al silicate, K-Al silicate (feldspar), Na-Al silicate (feldspar) Na-K-Al silicate (feldspar), $CaSO_4$, $PbSO_4$, apatite and pyrite are also detected.

The water solubility of two lots of reagent grade As_2O_3 was determined over the temperature range from 20 to 100°C. The solubility of As_2O_3 in water increases systematically with increasing temperature, and there is generally good agreement between in the data realized on heating and on cooling. Solubilities of up to 83 g/L As_2O_3 were noted, and these values agree closely with the published data for pure As_2O_3. It was further shown that all of the arsenic was present as As(III) throughout the duration of the experiments, which were done in air for periods in excess of 30 days. The solubility of reagent grade Sb_2O_3 was measured under similar conditions. The Sb_2O_3 is nearly insoluble over the entire temperature range from 25 to 95°C; the solubility at 25°C is <10 mg/L, and at 95°C, it is only 55 mg/L Sb_2O_3.

The solubility of As_2O_3 over the four As_2O_3-rich dust samples was also measured as a function of temperature on both heating and cooling. In all instances, the solubility of As_2O_3 over the dust, as determined during the heating cycle, is much lower than that determined over reagent grade As_2O_3. In fact, the solubility of any of the As_2O_3-rich dusts is only about one-half of that of pure As_2O_3, despite the ~3 day equilibration periods used at each temperature. Furthermore, there is a significantly different solubility measured on heating and on cooling. The solubility increases systematically on heating, but when the temperature is reduced, the solubility of As_2O_3 remains constant until the solubility curve for reagent grade As_2O_3 is intersected. As the temperature is reduced further, the solubility then follows the curve for reagent grade As_2O_3. The solubility of Sb_2O_3 over the four As_2O_3-rich dust samples was also determined. The measured solubilities are low; the solubility is always less than 160 mg/L Sb. The solubility of Sb determined on cooling is always higher than that realized during the heating cycle. The difference could indicate some oxidation of Sb (III) to Sb (V) during the experiments or it could reflect the strong tendency for the low concentrations of dissolved Sb_2O_3 to supersaturate in aqueous media.

There appears to be a correlation between the Sb content of the dusts and their As_2O_3 solubilities; high Sb contents result in lower As_2O_3 solubilities. The mineralogical studies of the four as-received As_2O_3-rich dusts showed that the solid solution Sb contents of the dominant As_2O_3 phase range from 0 to several percent. It is tentatively postulated that only the low-Sb As_2O_3 crystals dissolve readily in water at temperatures <100°C. Support for this hypothesis is provided by the fact that the As_2O_3 solubility increases when a very large excess of As_2O_3-rich dust is added to the reactor, and by the mineralogical studies of the leach residues which indicate a concentration of Sb-rich As_2O_3 particles in the leach residue.

The initial solubility studies indicated a low As_2O_3 solubility over the four As_2O_3-rich dusts at temperatures <100°C. Accordingly, the solubility was investigated at temperatures above 100°C using a titanium autoclave. Heating the As_2O_3-rich dusts to 125-200°C results in a significant increase in the solubility of As_2O_3, and this fact is the basis of a hot water leaching procedure proposed as one means of producing a marketable As_2O_3 product from the As_2O_3-rich dusts. The procedure consists of leaching the As_2O_3-rich dust in water for 2h at 150°C in an autoclave to dissolve a significant amount of the arsenic. The slurry is cooled to 95-100°C, and is filtered hot, but at atmospheric pressure. The clear As_2O_3-saturated liquor is cooled to room temperature to produce a significant yield of "pure" As_2O_3 crystals. Arsenic extractions of >95% seem possible. Under the preferred conditions, the As_2O_3 crystal product contains <0.1% Sb and <0.005% Fe. Mineralogical study of the hot water leach residues confirmed the dissolution of the low-Sb As_2O_3 crystals, but showed that the Sb-rich $(Sb,As)_2O_3$ phase remained in the leach residue. As anticipated, the leach residue also collects the various silicate and iron oxide species present in the original As_2O_3-rich dusts. Also, gold concentrates quantitatively in the leach residue, and its recovery is warranted.

During the leaching of the As_2O_3-rich dusts, some Sb co-dissolution occurs, and the co-dissolved Sb can contaminate the final As_2O_3 product. Consequently, efforts were made to remove the Sb from the aqueous solution using four ion exchange resins (Gravex GR-2-0, Amberlite IRC 120, Amberlite IRC 50 and Duolite C467) and activated carbon (Hycarb 6x12). Unfortunately, none of the ion exchange resins removed any significant amount of Sb from the water leach solutions at either 25°C or 95°C. The activated carbon removed ~25% of the Sb, but co-extracted major amounts of As as well. The negative results likely are a consequence of the absence of cationic antimony species in the near-neutral aqueous media. In contrast, cationic antimony species are present in acid media. Reducing the pH of the solutions to pH 3.0 had little effect on the extent of Sb extraction, but reducing the pH to 1.0 resulted in the removal of a significant amount of the dissolved Sb. In particular, the Duolite C467 resin extracted >90% of the Sb, and the extent of extraction likely could be increased by optimization of the extraction parameters. Although ion exchange holds little promise for the removal of Sb from near-neutral water leach solutions, it probably could be employed to purify the liquors generated in an acid leaching circuit.

Controlled re-sublimation of the as-received As_2O_3-rich dusts should enhance the purity of the As_2O_3 product and should completely reject the non-volatile oxide and silicate species. It was shown, in fact, that re-sublimation effectively rejects all impurities except for Sb. The Sb content of the re-sublimed As_2O_3 product increased as the temperature increased and as the duration of the re-sublimation tests increased. Oxidizing atmospheres (air or O_2 gas) yielded higher quality As_2O_3 products than the use of neutral (N_2 or He gases) or reducing (H_2 gas) atmospheres. A direct comparison of the thermal behaviour of the four As_2O_3-rich dusts was made by heating each dust at 545°C for 10 h in static air. There is a near-linear relationship between the As/As+Sb percentage of the As_2O_3 product and the As/As+Sb percentage of the as-received As_2O_3-rich dust. As anticipated, all of the initially present gold remains in the sublimation residue. The results reflect a persistent re-sublimation of Sb, despite the significant difference in the boiling points of Sb_2O_3 and As_2O_3. Limited mass spectrographic work done in support of the study, however, detected mixed arsenic-antimony vapour species, notably As_3SbO_6, in the vapours over the As_2O_3-rich dust. Such mixed As-Sb oxide species have a vapour pressure greater than that of end-member Sb_2O_3, and presumably account for the vapour transport of Sb, even at relatively low temperatures. Efforts to control the transport of Sb by the addition of metallic arsenic to the system were not especially successful. Supporting mineralogical studies of the re-sublimation residues detected major amounts of iron arsenate ($Fe_2As_4O_{12}$ or $FeAs_2O_3$ having a minor Sb content), $CaSO_4$, muscovite, chlorite and quartz. Less abundant species include Ca arsenate, Na-Al silicate, As-bearing iron oxide, a rare Fe-Zn arsenate phase, and possibly, elemental arsenic. Large masses of As_2O_3 were sometimes present, but these particles may have spalled from the walls of the reaction tube during sample collection. Overall, the re-sublimation studies indicate a persistent transport of Sb that may be difficult to control if rapid re-sublimation rates and high As_2O_3 product recoveries are sought.

A series of scoping tests was done to evaluate the possibility of enhancing the solubility of As_2O_3 over the as-received As_2O_3-rich dusts by using acid media in place of water. The presence of nitric acid, hydrochloric acid or sulphuric acid results in the rapid dissolution of As_2O_3 from the As_2O_3-rich dust, such that near-steady state solubilities are realized in less than 30 min. Furthermore, the extent of As_2O_3 solubility is greatly enhanced, relative to that in water. As expected, the solubility of As_2O_3 in acid media increases with increasing temperature, and with increasing initial pulp density to the point where solution saturation is achieved. Although the solubility of As_2O_3 increases slightly with increasing HCl concentration, it decreases with increasing HNO_3 concentration, for concentrations at least as high as 4.0 M HNO_3. The three acids tested yielded similar As_2O_3 solubilities, and their efficacy may be related to their ability to solubilize Sb. That is, it is believed that the acid solubilizes at least part of the Sb, thereby minimizing its "passivation" effect on the dissolution of As_2O_3. A negative consequence of this behaviour is the presence of relatively high Sb (and Fe) concentrations in the acid leach liquor. Fortunately, ion exchange resins can remove Sb from acidic media, and a number of techniques exist to control the dissolved Fe. Cooling of the hot acid leach liquors to 25°C resulted in the precipitation of large amounts of As_2O_3. Efforts to increase the yield of As_2O_3 crystals by neutralizing the solution after As_2O_3 crystallization were not successful. Only very amounts of an amorphous or poorly crystalline phase were formed when the solutions were neutralized to pH 9.0 with Na_2CO_3.

Overall, this study has shown that "pure" As_2O_3 can be produced from the As_2O_3-rich dust generated at the Giant Mine by using hot water leaching, acid leaching or re-sublimation techniques. The traditional problems associated with water leaching seem to have been overcome by the use of an autoclave to increase the leaching temperature to ~150°C. Of the three options considered, the hot water leach procedure seems to control impurities most effectively. Acid leaching offers advantages over water leaching with respect to the rates of dissolution, As_2O_3 solubilities and possible lower costs, because of the avoidance of autoclave processing. It suffers in that the Sb and Fe impurities in the As_2O_3-rich dusts are more extensively solubilized. Also, the effectiveness of this technique for more Sb-rich dusts requires demonstration. Re-sublimation of the As_2O_3-rich dusts effectively controls the oxide and silicate impurity species, but is much less effective in eliminating Sb. The present results suggest that it would not be possible to control Sb adequately during the re-sublimation of Sb-rich dust feeds.

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Note. All figures are missing from this report - downloaded from internet.