

GIANT YELLOWKNIFE MINES LIMITED
P.O. Bag 3000
Yellowknife, N.W.T.
X1A 2M2

FAX COVER PAGE

DATE: June 29, 1988TIME: 10:15 a.m.OUR REF. NO: GT3145ATTENTION: Ken BlowerFROM: Kent MortonNO. OF PAGES TO FOLLOW: 10 (Excluding This Cover Page)

COMMENTS OR INSTRUCTIONS:

The pilot plant is shut down awaiting replacement high temp. filter bags
(shut down Saturday evening). According to the schedule, the plant is not
due to resume operation until July 18. This should give RPC plenty of time
to make repairs and modifications. M. Chalkly sent the attached inspection
report. Condenser design problems have not yet been solved though I think
the proposed modification has a chance of working.

If there is a problem with this transmission, or if you wish to
contact us, following are our numbers:

Telephone: 403-873-6301 ext. 128
Fax: 403-873-2980
Telex: 034-45514

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Observations on Opening Pipework and Equipment

1. Fine brown dust in pipework. Loose, not adhering to surface. Particle size analysis of this dust is the same as for hot baghouse product indicating the likelihood of a tear in a bag rather than opening of the weave.
2. Vertical section of pipework almost completely plugged. The plug extended only 1/2" along horizontal section towards hot baghouse. This indicates that the heating tape was successful in keeping the wall temperature above the condensation temperature. The cooling effect of the cold air on the walls of the vertical pipework led to condensation on those walls. The conclusion is therefore that the hot and cold gases must be mixed in a section of large diameter so that condensation can take place in the gas phase rather than on a cold surface.
3. By lowering a weight into the condenser body and using an inspection mirror, I was able to view the gap at the top of the annulus. No buildup was present.
4. Extremely thin layer of white arsenic trioxide was observed on patches of these walls. These are of no concern.
5. The cone section was clean.
6. The annulus was plugged with hard material. we are attempting to remove the inner section from the outer section of the condenser and clear the annulus.
7. The pipework (horizontal section) between the condenser and the cold baghouse contained loose arsenic trioxide. In general the material was white with streaks and patches of brown. This would indicate an intermittent contamination with impurities, possibly coincidental with hot baghouse blowback.
8. The entrance to the cold baghouse was clear.

Plans

1. Attempt to clear annulus so that cold air can be introduced through annulus and hot air through top of condenser.
2. Install heating coils on vertical pipework above condenser (section that was plugged) and part way along horizontal section towards hot baghouse.
3. Increase diameter of vertical pipework above condenser so that an insulated cold air lance can be inserted. The insulation is to ensure no cold surface above condenser body. A schematic is shown on the next page. The cold air is introduced through a 1/2" dia stainless steel pipe, surrounded by a mouldable, insulating refractory sleeve which in turn is encased in a 2 1/2" dia stainless steel pipe which will be tack welded to the inside of the top flange. A thermocouple will be located

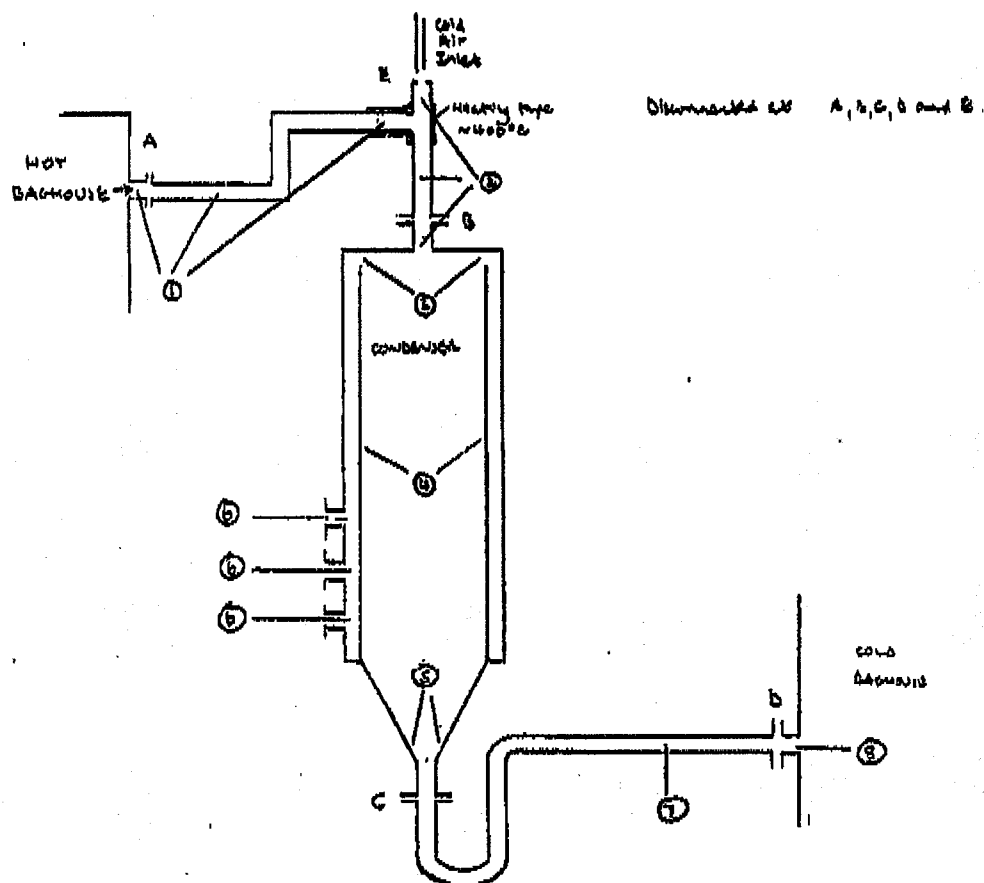
between the outer surface of the refractory and the inner surface of the 2 1/2" pipe. This temperature must be above 350 deg C to ensure that no condensation will take place above the condenser chamber. This setup can be pulled during preheating, prior to feeding baghouse dust and will provide an alternative to introducing cold air through the annulus.

4. Remove top of hot baghouse and remove bags for inspection and replacement.

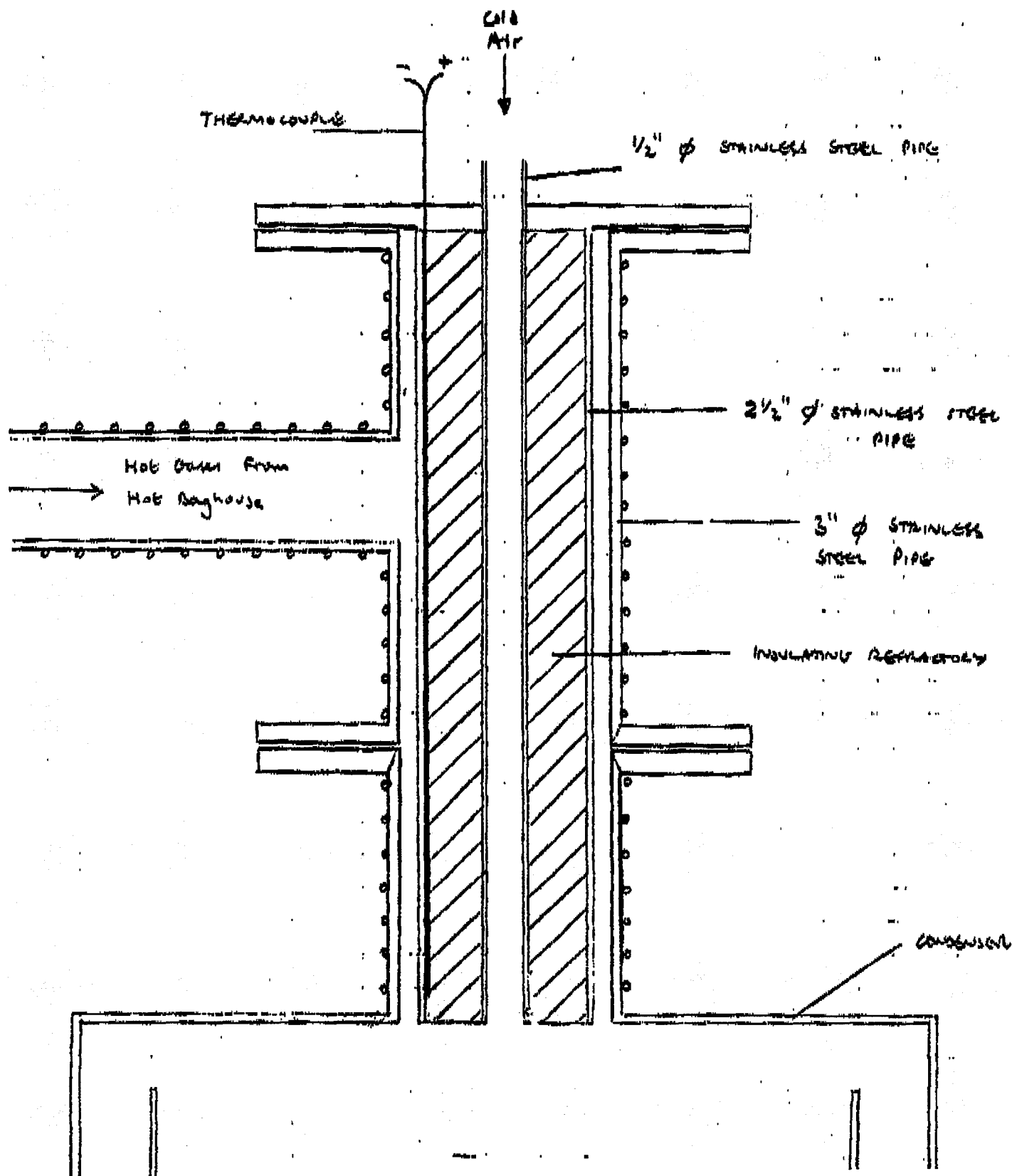
5. Modify screw feeder to give thicker teflon sleeve and minimize backflow of transport air to feed hopper.

6. Referring to the schematic diagram of the cold air lance, we have a concern that plugging may occur around the tip of the lance. We will therefore consider the alternative of having a heated lance, with hot gases passing down the center of the lance and cold gases around the outside. When considering these alternatives, the most promising method of introducing the gases to the condenser would appear to be cold air through the annulus and hot gas through the top, perhaps via a heated lance. It is important to have a number of options available to us.

I believe that the reason that we are having problems with mixing hot and cold gases and you don't seem to have that problem in your operation is simply due to the scale of the operation.



COLD AIR LANCE



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rpc

research and productivity council
conseil de recherche et de productivité

Hi

For your info

Fax Ref. # 403-873-2980

And

FAX NUMBER IS (506) 452-1395

FAX INFORMATION SHEET

TO: K. Morton DATE: June 29, '88 TIME: 12:00 pm
COMPANY: Giant Yellowknife
FROM: Mike Chalkley
SUBJECT: ARE ANSONIC TRUCKING AGREEMENT

COMMENTS: INTERESTING PAPER - I'M NOT SURE THAT I AGREE
WITH SOME OF THE COMMENTS

TOTAL NUMBER OF PAGES INCLUDING THIS COVER SHEET 7

THIS TRANSMISSION IS BEING SENT TO YOUR OFFICE BY A NEFAX PF-1 MACHINE. IN THE EVENT YOU SHOULD EXPERIENCE TROUBLE RECEIVING OUR TRANSMISSION, KINDLY CONTACT OUR OFFICE AT (506) 452-8994.

SIGNED: 

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Commission Eur. Comm., Jt. Res. Cent. Espos, Italy Chapter 6
1982 (Eur. 7624)

RECOVERY OF HIGH-PURITY ARSENIC TRIOXIDE FROM ARSENOPIRYRITE

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ABSTRACT

Treatment of tungsten ore at Anschutz Mining Company's Chicote Grande (Bolivia) operation results in a relatively high grade arsenopyrite byproduct stream. Laboratory and miniplant testwork have been performed at Colorado School of Mines Research Institute to examine the arsenic product from this source. The selection was constrained by the remote location of the millsite, which demands an uncomplicated, low maintenance operation.

As a result of the research effort, a two-stage roasting/condensing process was developed, featuring the use of an indirect heating method. Arsenic was efficiently extracted and the arsenic trioxide (As_2O_3) product consistently exceeded the industrial purity specification of 99.5%. Key process parameters have been secured for extrapolation of the process to pilot or small commercial scale.

INTRODUCTION

Growing environmental, health, and safety constraints have combined to create an expanding burden of cost and inefficiency in the production of various toxic metal oxides. In particular, the production of arsenic trioxide has been especially adversely affected.

With the declining production of arsenic trioxide by simple pyrometallurgical methods and the growing complexity and cost of production through more recent hydrometallurgical techniques, novel and environmentally responsible processes are required.

One approach capable of mitigating some of the problems of high gas velocities, subsequent dust escape, and material handling - all common to the simpler pyrometallurgical techniques, is that of indirect roasting. This method allows for close reaction temperature control, easier gas condensation and cleaning and minimal problems with dust excursions.

recovery of arsenic in the form of a high-purity arsenic trioxide powder from arsenical sulfide minerals has recently been completed at the Colorado School of Mines Research Institute. The program was initiated to determine the technical feasibility of producing the arsenic trioxide as a by-product of Anschutz Mining Company's Chicote Grande tungsten operation, located in the Bolivian Andes near Oruro.

Through its Bolivian subsidiary, Churquini Enterprises, Anschutz currently operates a small capacity mine and mill for the recovery of a tungsten (wolframite) concentrate. The present concentration process uses a combination of gravity and froth flotation techniques to produce a 74 percent WO_3 concentrate. In addition to wolframite, the Chicote ores contain an appreciable concentration of arsenic in the form of arsenopyrite ($FeAsS$). The wolframite concentration process also acts to create a sulfide waste stream containing an average of twenty to thirty percent arsenic.

Rather than continue to discard this material as waste, a means of recovering the arsenic as a marketable by-product was sought. All studies indicated a high-purity arsenic trioxide powder to be the product that would allow the most favorable marketing situation.

Since the site for the proposed operation is a remote area in Bolivia, it was desired that the recovery process be rugged, uncomplicated and environmentally responsible. Also influencing the selection of the extraction method was the requirement that the process be amenable to treating the tungsten concentrates for arsenic removal on an intermittent basis.

A number of procedures for the elimination, retention, or extraction of arsenic through roasting pyritic ores or concentrates are described in the literature. Occasionally, as in the case of the operation at Giant Yellowknife, these processes are specifically designed for recovery of an arsenical product. More often, the element is removed as a consequence of a purification procedure for another metal and

environmental problem.

Currently, ASARCO is the major producer of arsenic trioxide in the United States. ASARCO processes arsenical dusts and ores in their Tacoma, Washington smelter facility. Their process and its foreign counterparts such as Boliden rely on by-product or waste streams from the processing of ores or concentrates for other metal values as a source of arsenic. Many of these operations share the disadvantage of operation in the batch mode. Other facilities such as the aforementioned Giant Yellowknife operation rely primarily on hydrometallurgical processing methods.

After assessing all practical methods of extracting and refining the arsenic, it was decided to employ an indirectly-heated roasting technique. It was hoped that by using such a scheme that the pollution control equipment requirements could be minimized as a result of the low offgas volume.

The Colorado School of Mines Research Institute was selected to perform the study and was instructed to utilize the simple pyrometallurgical approach. The study was authorized to demonstrate the technical feasibility of producing such a high-grade product from the Bolivian concentrates on laboratory and mini-plant scale. Further work was to be performed to delineate basic process parameters and to collect the necessary data for future pilot and commercial scale operations.

EXPERIMENTAL

The focus of the study was the determination of optimum roasting parameters for high efficiency volatilization and recovery of arsenic from Chicote arsenopyrite concentrate. The primary variables of interest in this undertaking were temperature, residence time and furnace atmosphere.

Materials

Five samples were obtained from the Chicote operation for the laboratory and mini-plant tests. The composition of each sample is indicated in Table 1.

Table 1. Chemical Analysis of Samples Used for Arsenic Extraction Process Development

Sample No.	S, %	As, %	Fe, %	WO ₃ , %
1.	28.0	4.4	-	-
2.	17.3	42.5	33.4	-
3.	-	44.4	-	-
4.	19.6	27.3	35.2	12.6
5.	0.1	0.1	16.7	73.5

As indicated in Table 1, sample No. 1 has very low in arsenic content in comparison with the

other samples. This sample was drawn from the sulfide flotation operation in the Chicote concentrator. Inspection of the arsenic content of samples number 2 and 3 indicates that they approximate pure arsenopyrite, FeAsS. The fourth sample was considered to be a "confirmatory" blend of flotation concentrate and table product in the approximate proportion expected at the mill. Finally, a sample of arsenic contaminated (0.13% As) wolframite concentrate was procured to test the effectiveness of the roast procedure for concentrate purification.

Sample number one was used only in the preliminary laboratory investigations. Samples two and three were given more extensive consideration on both the laboratory and pilot plant scale as they provided the bulk of the raw material used throughout the test program. Finally, the fourth or "confirmatory" sample was used to produce refined arsenic trioxide in bulk quantities once the optimum roasting parameters were established.

The arsenopyrite concentrate samples were received as essentially one centimeter lumps, whereas the confirmatory sample was of finer grain size at approximately ninety-seven percent passing 6.7 mm. The samples were crushed to minus 1.7 mm, blended, and split to obtain uniform samples for analysis and testing.

Preliminary Testing A series of preliminary laboratory scale scoping tests were arranged to examine the effects of varying temperature and furnace atmosphere on the degree of arsenic volatilization for the arsenopyrite samples. Each of the four arsenopyrite samples was independently tested in the laboratory roasting apparatus which consisted of a Vyser reaction tube within a small tube furnace. Initially, testing had been attempted in a small muffle furnace, however, this practice proved impractical because of difficulties encountered in recovering the arsenical fumes and in controlling the furnace atmosphere.

In each test, a small charge of the crushed arsenopyrite concentrate was placed in a porcelain reaction crucible which in turn was centered in the reaction tube. A thermocouple was placed inside the reaction tube, above the concentrate, to monitor roast temperature. Furnace atmosphere was maintained at an oxidizing, inert, or reducing condition by continuous injection of air, nitrogen, or carbon monoxide, respectively. Both ends of the tube were kept gas-tight. Offgases were withdrawn from the reaction tube and pulled through a water-cooled condenser in order to effect product recovery. The entire system was operated under a hood to prevent any leakage of arsenic fumes to the laboratory atmosphere.

The low grade Sample No. 1 responded best under conditions of an inert atmosphere at a minimum temperature of 650°C. However, the other three samples (Nos. 2 through 4) exhibited superior arsenic extraction efficiencies with an oxidizing (air) atmosphere and a minimum roasting temperature

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ARSENIC TRIOXIDE RECOVERY FROM ARSENOPYRITE

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of 850°C. Since the actual analysis of the concentrate is expected to most closely resemble that of Sample No. 4, these results were used to design the miniplant.

Analysis of the condensed product indicated that the arsenic powder recovered from these extraction tests required a second volatilization and condensation stage to reach the desired level of purity. The revolatilization roast was performed at a temperature of 400°C using the same apparatus as described above. Analysis of the second product was satisfactory as the purity of the powder exceeded 99.5 percent arsenic trioxide.

Subsequent to identifying general parameter ranges on laboratory scale, roast/condensation experimentation was performed in a specially constructed continuous roaster and condenser circuit.

Miniplant Equipment Description The apparatus used for the miniplant study was constructed of a combination of stainless and mild steel components. The basic roaster design provided for a variable-speed drive screw conveyor to withdraw the dry arsenopyrite concentrate from a sealed feed bin. This conveyor discharged the concentrate through a short vertical section to a second variable-speed driven screw conveyor which transported the ore through the roasting section.

The roasting section and all ducting between principle components had a 5.1 cm internal diameter. The roasting section consisted of the second screw conveyor concentric within a 15.2 cm (internal diameter) steel tube. Roaster heat was provided indirectly, by burning natural gas in a separate furnace with the combustion products passing through the 15.2 cm tube and then withdrawn to exhaust. Air for the vapor sweep through the roasting section was drawn through a flowmeter by an aspirator located at the final gas outlet of the system. Airflow was concurrent with the concentrate flow through the roaster.

After passing through the roasting section, the solid residue was discharged by the screw conveyor into a sealed cylindrical cooling chamber, measuring 30.5 cm in diameter by 22.9 cm in height.

The arsenical roaster offgases were withdrawn from the roasting section through an externally heated electrostatic precipitator. This unit was a simple, unbaffled, round chamber measuring 15.2 cm in diameter by 30.5 cm in height. A center mounted electrode gave a dust passage width of 7.6 cm over an effective distance of approximately 20 cm.

A condensation chamber with water-cooled plates positioned as top-mounted baffles served to condense and recover the arsenic trioxide product. This chamber was of mild steel construction, measuring 30.5 cm in width by 30.5 cm in height by 28.1 cm in length.

Finally, the cooled gas stream was cleaned in a small venturi scrubber system before discharge. The entire roasting and condensing system was operated under negative pressure to prevent leakage of the arsenic fumes into the working area.

In order to ensure adequate temperature control in the system, temperature measurements were obtained by thermocouples located in thermowells at the following locations:

1. At the input of the burner gases to the heated zone of the roaster.
2. At the exit of the burner gases from the heated zone of the roaster.
3. In the residue discharge path at the end of the heated zone of the roaster.
4. In the vapor path just prior to the electrostatic precipitator.
5. In the vapor path between the electrostatic precipitator and the condensation chamber.

Miniplant Testing Procedure Prior to initiating the testing sequence, solid transfer rates were established for the upper and lower screws for each sample. At the start of each test, all heating elements were turned on, the gas burner was ignited, reaction chamber screw was started, and the system was brought to equilibrium at the desired temperature. All vapor areas were kept at temperatures above 450°C to prohibit the condensation of arsenic trioxide in areas other than the condensing chamber. Water was allowed to circulate through the plates in the condenser, and the aspirator was started at the beginning of the heat-up period to maintain negative pressure throughout the system.

The general testing procedure started after the total system reached steady-state temperature. Also, during the majority of the test runs, the burner offgas was analyzed for oxygen to ensure efficient combustion.

The crushed concentrates were fed to the roast apparatus by a double choke fed screw conveyor. This design was implemented to prevent back-burning of the concentrates to the feed bin. The second screw conveyor fed the roast chamber at a reasonably uniform rate. Feed rates were adjusted by means of a variable speed drive to attain furnace retention times of 3.0 to 10.0 minutes. Other variables included the roast temperature (650 to 850°C) and the airflow through the reactor (0 to 15 liters per minute).

The residue was transported through the reaction chamber by a screw device, dropping (after the roast) into a sealed residue container. Offgases advanced to a "hot" electrostatic precipitator for removal of entrained particulate. An air inlet was provided in the residue drop line to ensure a flow of gas away from the residue storage and to provide oxygen necessary for the

*installed J
hot baghouse*

condensation of the trioxide product. *why?*

The first feed through the reaction chamber was removed from the residue collection box and discarded. Residue was collected over the test period (usually several hours at equilibrium). The residue removed from the collection box was analyzed for arsenic in order to determine the amount volatilized.

After passing through the hot electrostatic precipitator, the gases were introduced to a water-cooled condensation chamber. Virtually all of the arsenic was condensed as a fine white arsenic trioxide powder. The quality of the product was limited to approximately 90 percent purity, primarily because of the inefficiency of the electrostatic precipitator used in these tests.

The arsenic-depleted gas stream was withdrawn through a second, larger settling chamber, then scrubbed with water to remove any entrained solids. To ensure a safe working environment, the entire system was operated under negative pressure.

Residue samples were retrieved and analyzed to determine the arsenic extraction efficiency. Arsenic trioxide product was collected for analysis and to provide raw material for the purification tests.

Purification Procedure The reactor was thoroughly cleaned and heated up to the same operating temperatures used for the arsenopyrite, and the feed hopper filled with crude arsenic trioxide. The crude products were loaded into the feed bin and the apparatus was generally operated as with the arsenic concentrates. The crude arsenic trioxide was put through the roaster and collected in the condensation chamber as normal, the only critical difference being the roasting temperature which was evaluated over the range 350° to 540°C. The final purified products were removed from the chill box, well blended, and analyzed for purity and bottled for potential customer inspection.

RESULTS AND DISCUSSION

In the first test series with the arsenopyrite, the effect of variable temperature was evaluated. A ten minute retention time in the roasting section, and the total air flow of twenty liters per minute were held constant. Preburner exhaust gas was analyzed periodically for excess oxygen to ensure complete combustion of the natural gas fuel. The residue recovered over a fixed period of time at equilibrium conditions was weighed and analyzed for arsenic in order to determine extraction efficiency. The results of this series of tests are summarized in Table 2.

Table 2. Results of Variable Temperature Test Series.

Roaster Temperature °C	As in Residue %	As Volatilization %
650	30.1	29.2
700	4.6	89.2
750	9.4	78.0
850	3.4	91.9

The data generally indicates that a temperature in excess of 700°C is effective in achieving approximately ninety percent arsenic volatilization. However, in order to keep the entire system at temperature and prevent premature condensation of arsenic oxides, a standard roast temperature of 850°C was necessary. The results of the test conducted at 750°C were judged anomalous because of extensive operating problems (primarily mechanical in nature) that were encountered during the course of that particular test.

The variable of solids retention time in the roasting section was next considered. To study this effect, the roaster temperature was fixed at 850°C and the arsenopyrite feed was introduced at rates corresponding to roaster retention times of 3.0 to 10.0 minutes. The total air flow through the roaster was again held constant at twenty liters per minute. The results of this test series are presented in Table 3.

Table 3. Results of Variable Retention Time Test Series.

Residence Time min.	As in Residue %	As Volatilization %
10.0	3.43	91.9
7.5	4.08	90.4
5.0	4.86	89.0
3.0	7.40	83.2

The results indicate that the residence time in the roasting zone should be at least five minutes to achieve the desired arsenic extraction of ninety percent.

Confirmatory Samples A sample of "confirmatory" arsenopyrite concentrate was tested under the similar conditions as has been used for the other samples. The exact conditions selected were a roaster temperature of 850°C and a residence time of ten minutes. Air flow was selected as the major variable in this test series. The results of these tests are summarized in Table 4.

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Table 4. Results of Variable
Airflow Test Series.

Air Input liters/min.	As in Residue %	As Volatilization %
5	8.15	70.0
5	2.65	90.0
10	1.31	95.2
10	0.98	96.4

The data indicates that arsenic can be effectively volatilized from the confirmatory sample with an air input to the roaster of between five and ten liters per minute, using the conditions specified above for temperature and retention time.

Purification of the Crude Arsenic Trioxide Product

The crude arsenic product recovered from the extraction tests was treated in the same experimental apparatus as was previously described for the extraction roast. It was found that the volatilization procedure required a roast temperature of 450°C to completely evolve the crude arsenic trioxide. Minimal amounts of solid residue were recovered from the roaster discharge. The analysis of the purified product easily met the consumer purity specifications.

The analysis, reproduced in Table 5, indicated that the purity of the final product exceeded the specified level of 99% arsenic trioxide.

Table 5. Chemical Analysis of Purified
Arsenic Trioxide.

Element	Percent (by weight)
As ₂ O ₃	99.95
Fe	0.001
Sb	0.002
Pb	0.001
C	0.001

The only problem encountered, save for the well expected mechanical failures, occurred during an early attempt to reprocess the crude arsenic trioxide from the confirmation concentrate at temperatures lower than 400°C. A problem was encountered with the formation and excessive buildup of a vitreous product along the walls of the testing apparatus. Analysis of this product revealed it was arsenical and thus it was proposed that the problem was due to a combination of moisture cooling and lack of oxygen (necessary for the formation of arsenic trioxide) in the testing chamber.

Arsenic Removal from Tungsten Concentrate The effectiveness of the system in purifying the arsenic-contaminated tungsten concentrate was

tested using the optimum parameters determined by the studies involving the arsenopyrite concentrate. The procedure reduced the arsenic content of this concentrate sample from 0.13 percent down to 0.05 percent.

CONCLUSIONS

The technical feasibility of producing a marketable high-purity arsenic trioxide powder was successfully demonstrated through the use of the miniplant. Process parameters have been obtained that are suitable for the design of a continuous pilot plant or perhaps a small commercial facility. However, it is expected that testing will take place on a larger scale than reported herein prior to commercial scale-up in order to ascertain the data.

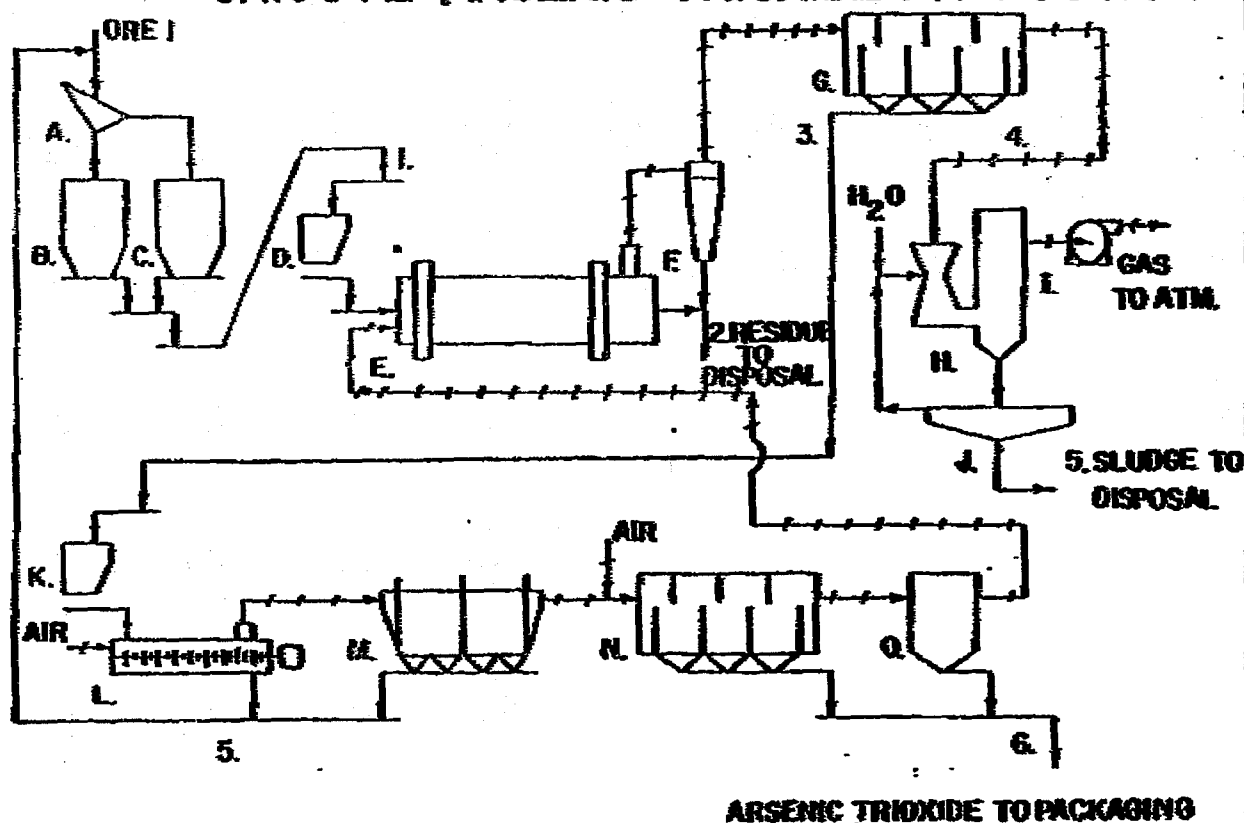
The next step in the testing progression is to advance to pilot plant scale to ensure the viability of the process utilizing commercially available process equipment. The groundwork for this effort has been set. The extraction roast will again utilize the indirect heating method as testing is planned for an indirect-fired rotary calciner. The choice of equipment available for a purification (if required) is much greater since the operating temperature for the volatilization of the crude arsenic product is substantially lower. Tentative plans have been made to effect the volatilization roast in a pug mill heated indirectly using a heat transfer fluid.

A primary consideration in the next set of tests will be the determination of whether the purification step is truly necessary to achieve the consumer specifications for the arsenic trioxide powder. Observations recorded during the extraction phase of the testing suggested that a more efficient and reliable hot electrostatic precipitator may increase the quality of the first generation arsenic trioxide condensate sufficiently to eliminate the need for the volatilization stage.

Continued regulatory and financial pressures will eventually push this process technology toward commercialization. Growing uses for arsenic compounds and continued declines in productive capacity provide the necessary impetus to pursue commercial development.

has
baghouse?

CHICOTE ARSENIC TRIOXIDE PRODUCTION



PRELIMINARY MASS BALANCE

STREAM NO.	SOLIDS (KG.)	ARSENIC		IRON		SULFUR		INERTS (KG.)
		(KG.)	(%)	(KG.)	(%)	(KG.)	(%)	
1	10,000	4,250	42.5	3,340	33.4	1,750	17.5	660
2	5,727	142	2.5	3,333	58.2	637	11.1	658
3	5,413	3,546	73.0	139	2.5	265	0.5	274
4	285	208	73.0	7	2.5	14	0.5	2
5	232	—	—	139	59.9	265	11.4	274
6	5,152	3,900	75.7	—	0.001	—	0.001	—

Figure 1. - Preliminary Process Flow Diagram and Material Balance for Chicote Grande Arsenic Trioxide Production.