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FALCONBRIDGE NICKEL MINES LIMITED

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INTER OFFICE MEMORANDUM

MEMO TO: W.A. Moore

FROM: W.R. Hatch

DATE: November 29, 1979

SUBJECT: Solubility of Arsenious Oxide at Elevated
TemperaturesPROJECT No. 201-791129

JO#2484

KEYWORDS: Pressure Leaching, Baghouse Dust,
Giant Yellowknife Gold Mines

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ABSTRACT

A preliminary investigation has been carried out on a pressure leach-crystallization process for the purification of arsenious oxide from Giant baghouse dust. Pressure leaching tests have established the solubility of As_2O_3 at 177 g/L at 154°C and a complete solubility curve is given based on experimental work to date.

Rate studies have been difficult to carry out under present autoclave design but preliminary data indicates a residence time of 15 min is required to reach the solubility limit.

Recycle leaching has produced high yields of product (>98% As_2O_3) containing impurities within specification. Silica and iron values are higher than that obtained in atmospheric leaching whereas antimony values are lower. Possible explanations are given.

Due to the greater yields of As_2O_3 and the indicated lower energy requirements of the process it is recommended that additional laboratory tests be carried out to define reaction rates and that the leaching crystallization process be examined in mini plant scale operation at Giant.

INTRODUCTION

The purification of arsenious oxide from Giant baghouse dust is currently under investigation. As requested in your memorandum of Nov. 2, 1979 we have examined various phases of the high temperature-pressure leaching of Giant baghouse dust.

(INTRODUCTION, Cont'd.)

Various figures are reported in the literature for the solubility of As_2O_3 at different temperatures. Conflicting values are reported from various sources which apparently stem from the fact that arsenious oxide can exist in three allotropic modifications, claudetite (monoclinic), arsenolite (cubic) and an amorphous glassy modification. The rate of dissolution can be extremely slow in some cases, this depending to a great extent on the actual particle size of the material in question.

Giant baghouse dust is known to be extremely fine and only the cubic arsenolite (As_4O_6) has been identified by X-ray diffraction studies(1).

Much of the data on Arsenolite solubility originates with the work of Anderson and Story(2). These values cover the temperature range 0-98.5°C and are given in Figure 2. The only values known to the author above 100°C are those reported in the Japanese patent and which are given in Figure 2 (3). These values were obtained in leaching tests on reagent grade (200 μ) arsenious oxide. The essential features of their process were summarized in our original literature survey(4).

EXPERIMENTAL

A number of preliminary autoclave tests were carried out in a 2 litre autoclave. Giant baghouse dust sample 79-439 (A7686) was used which analyzed 94.1% As_2O_3 and 0.37% Sb.

The main problems to be overcome in the experiments were the liquid/solid separation. Fine particulate As_2O_3 had to be separated from the saturated solution, ensuring also that crystallization of the As_2O_3 did not occur.

The apparatus used in the test is shown in Figure 1. The procedure used in these tests was to charge the autoclave with a slurry of baghouse dust in water with an approximate 50% excess of As_2O_3 above that required for solution at the temperature desired. The autoclave was sealed and heated to temperature with stirring. The temperature was maintained constant ($\pm 2^\circ\text{C}$) for a period of 30 minutes by controlling power to the heaters and cooling water flow.

The stirrer was then stopped and the slurry was allowed to settle for a period of 10 minutes. The temperature was taken using a potentiometer and the solution was sampled.

Sampling was carried out through a coarse glass frit which was suspended well above the bottom (≈ 7.0 cm) of the autoclave. The saturated solution passed through a hot copper tube and valve assembly and was discharged into a weighed amount of cold distilled water contained in a graduated cylinder. After collecting about 25 g of saturated solution the contents were further diluted to between 100 and 250 mL, weighed and filtered immediately through a dry filter. Filtrate was analyzed for arsenic volumetrically by the iodometric method.

(EXPERIMENTAL, Cont'd.)

Test #129 was carried out using recycle As_2O_3 solution and baghouse dust at a temperature of 137°C . Three samples were taken after a 0.5 hour settling period.

Test #130 was carried out using water and high purity As_2O_3 obtained from Struthers Wells pilot tests. After 0.5 hours at a temperature of $154\text{--}160^\circ\text{C}$ the solution was allowed to settle for 0.5 h before sampling.

Test #132 was a larger scale test carried out at 137°C dissolving baghouse dust in water. Leaching time was 30 min and settling time was 10 min after which time 760 mL of solution was discharged into a closed reaction vessel. Crystallization was allowed to take place overnight and the crystals were separated. Overall solubility was calculated from crystal weights and solution analysis.

Test #133 was carried out with recycle solution and baghouse dust at 138°C . In this test 1300 mL of solution was discharged and crystallized after 0.5 hour leaching and 10 min settling periods.

Test #135 included two solubility measurements carried out on baghouse dust in recycle solution at 60° and 80°C at atmospheric pressure. Samples were taken after 1, 2 and 3 hours.

RESULTSSolubility of As_2O_3 at Elevated Temperatures

The results obtained from these tests are given as follows:

<u>Test No.</u>	<u>Temperature °C</u>	<u>As_2O_3 (g/L) In Each Sampling</u>	<u>As_2O_3 (g/L) Average</u>
T129	137	135 136 140	137
T130	154	177 177 169	174
T132	140	139	139
T133	138	152	152
T135	60	36.6 36.2 36.9	36.6
T135	80	46.7 44.7 45.2	45.5

(RESULTS, Cont'd.)

The values are plotted in Figure 2 along with values previously determined in experimental leaching tests on Giant baghouse dust as follows (4) (5):

<u>Temp. (°C)</u>	<u>As₂O₃ (g/L)</u>
10	17
20	18
85	52
95	61
100	70

Solubility values from Seidell and from A. Eiichi(3) are also shown in Figure 2.

RATE OF DISSOLUTION OF As₂O₃ FROM BAGHOUSE DUST (2)

Previous rate determinations have been carried out at 85°C and 95°C on Con As₂O₃ material. The solubility of As₂O₃ after 15 min leaching was within the experimental error of the value obtained after seven hours. The extremely rapid rate of solution is attributed to the very fine particle size.

Test #134 was carried out to estimate the rate at which As₂O₃ dissolved from baghouse dust at 160°C. The slurry was preheated to 95°C and then transferred to a superheated autoclave. Fifteen minutes were required to take the temperature from 95 to 160°C. The solution was above 154° approximately 5 minutes before sampling. Two samples were taken, after which further sampling was impossible due to plugging of the lines with As₂O₃.

RESULTS AND DISCUSSION

The two solutions sampled at 157 ±3°C analyzed 141 g/L As₂O₃ and 148 g/L As₂O₃ (Average 145 g/L As₂O₃). The value from the solubility curve should have been 186 g/L As₂O₃. A better experimental technique is required to rapidly raise the temperature and determine the rate of dissolution at elevated temperatures. A preferred method would be to heat the recycle solution to 160°C and then introduce the baghouse dust at temperature. Equipment modifications are required. Nevertheless this single test indicates fairly rapid dissolution rates and one could roughly predict a dissolution time of 15 min for saturation.

We do not know whether the dissoltuion rate at 160°C is more rapid than that at 100°C since saturation was attained at the first sampling time of 30 min in previous testwork.(4)

RECYCLE AUTOCLAVE LEACHING-CRYSTALLIZATION TESTS

An initial crystallization test was carried out (T-131) on 140 g of solution discharge from the autoclave. As_2O_3 was crystallized overnight in a stirred reactor and the crystals were weighed and analyzed. No overall balance was carried out on this leach-crystallization test due to the small amount of solution discharged from the autoclave. Crystal product (A8333) was retained for analysis.

Tests T132 and T133 were large scale recycle leaching-crystallization tests carried out at 137°C . In T132, 311 g of baghouse dust was dissolved in 2 litres of water for 0.5 hours. After settling, 800 mLs of solution were withdrawn and crystallized overnight to a final temperature of $\approx 23^\circ\text{C}$. Crystals were filtered off and mother liquor and crystals analyzed.

The residue from the autoclave containing insolubles and crystallized As_2O_3 was filtered off and the solution used for recycle leaching in T133 along with crystallizer mother liquor.

These combined recycle solutions totaling 1610 mLs were made to 2000 mLs with water and used in T133, adding 250 g of baghouse dust. Leaching conditions and crystallization was the same as in T132. The final residue and slurry filtrate were analyzed for As_2O_3 .

RESULTS

The As_2O_3 balances for the crystallization in T132 is as follows:

A8334 Crystallizer Mother liquor (760 mL at 44.2 g/L) = 33.6 g As_2O_3

A8335 Crystallizer Product As_2O_3 (77.5 g at 99.5% As_2O_3) = 77.1 g As_2O_3

Total = 110.7

The balance for T133 is given below:

<u>In</u>	- 1610 mL Recycle Solution at 44.2 g/L	71.2 g As_2O_3
	250 g Baghouse Dust at 94.1% As_2O_3	<u>235.3</u> g As_2O_3
		306.5 g As_2O_3
<u>Out</u>	- Crystals of As_2O_3 (153 g at 98.8% As_2O_3)	151.0 g As_2O_3
	Mother Liquor (1300 mLs at 45.2 g/L As_2O_3)	58.7 g As_2O_3
	Slurry Filtrate (750 mLs at 56.4 g/L As_2O_3)	42.3 g As_2O_3
	Residue (71 g at 80.9% As_2O_3)	<u>57.4</u> g As_2O_3
		311.5 g As_2O_3

(RECYCLE AUTOCLAVE LEACHING-CRYSTALLIZATION TESTS, Cont'd.)

The analysis of the As₂O₃ crystal products are given in the following Table.

<u>Sample</u>	<u>Test</u>	<u>As₂O₃</u>	<u>Sb</u>	<u>Fe</u>
A8333	131	99.2	0.015	0.032
A8335	132	99.5	0.039	0.019
A8339	133	98.8	0.077	0.031

The spectrographic qualitative analysis (Report Q-841) is given in the following Table.

<u>Concentration Range</u>	<u>Element in Sample</u>		
	<u>A8333</u>	<u>A8335</u>	<u>A8339</u>
0.03 - 0.3	Si	Si	Si
0.003 - 0.03	Fe,Mg	Fe,Mg	Fe,Mg
0.001 - 0.01	Al,Sb	Al,Sb	Al,Sb
0.0001 - 0.001	Ca,Ni	Ca	Ca

The purity of the products is satisfactory in that all contained +98% As₂O₃. Antimony is lower than in products obtained from atmospheric leaching but appears to be increasing as recycle leaching is carried out. Iron is slightly higher than obtained previously. It is thought however that this slight increase in concentration is not due to iron solubility since the pH was above 4.0, but to physical contamination originating from the use of a coarse glass filter in the liquid/solid separation.

Silica concentrations are an order of magnitude higher in these products (0.03 - 0.3) as compared to previous crystal products (0.003 - 0.03) and it appears that dissolution of silica may be occurring. More accurate chemical analysis is required but the level indicated does not appear detrimental as far as product specification is concerned.

CONCLUSIONS AND RECOMMENDATIONS

The high temperature leaching tests carried out on Giant baghouse dust indicate that a 200 g/L As₂O₃ concentration can be obtained at 160°C. The incremental amount of As₂O₃ solubilized for each 10°C rise in temperature is shown in Figure 3. The incremental equilibrium concentration is low and constant up to 70°C after which there is a steep rise in the curve. It is evident that maximum utilization of thermal energy can be obtained in a process operating between 160°C in the leach and 60°C in the crystallization stage, recovering about 160 g As₂O₃ per litre per cycle.

(CONCLUSIONS AND RECOMMENDATIONS, Cont'd.)

The dissolution rate of arsenious oxide in baghouse dust is rapid, reaching equilibrium concentrations in about 15 minutes at 140°C. Further dissolution rate tests are indicated.

The arsenious oxide crystallizes out as arsenolite (As_4O_6) of high purity (>98% As_2O_3). Some minor differences are noted particularly with Si, Fe and Sb and additional recycle leaching tests are warranted to establish impurity levels.

It is recommended that additional rate dissolution tests be carried out at FML and that the pressure leach-crystallization be tested in a mini plant scale of that conceived for commercial production. The later would best be accomplished at Giant.

W. R. Hatch

WRH/lm
Attach.

W.R. Hatch

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FIGURE 1: Autoclave - Sampling System

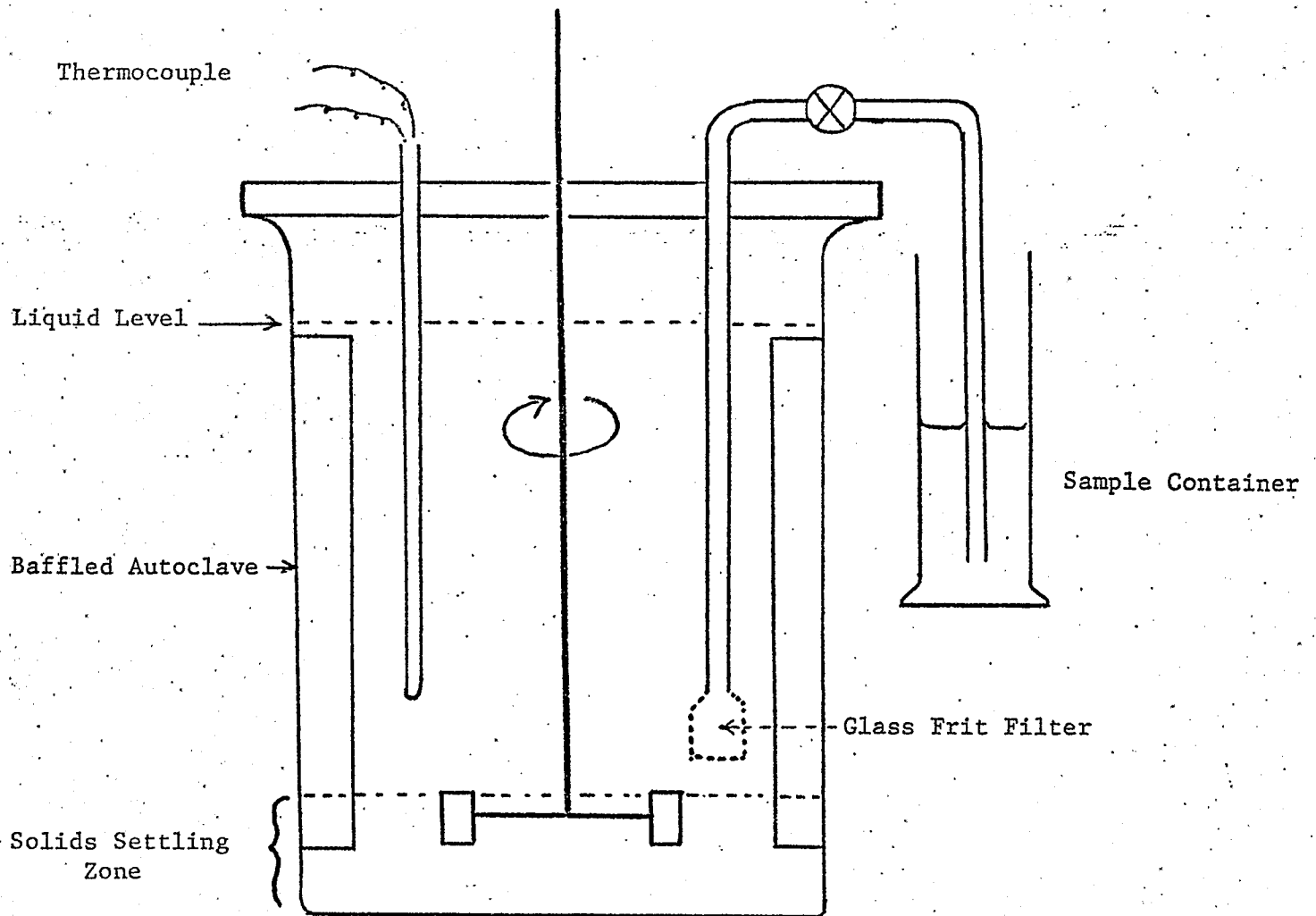


FIGURE 2: Solubility of Arsenious Oxide at Elevated Temperatures

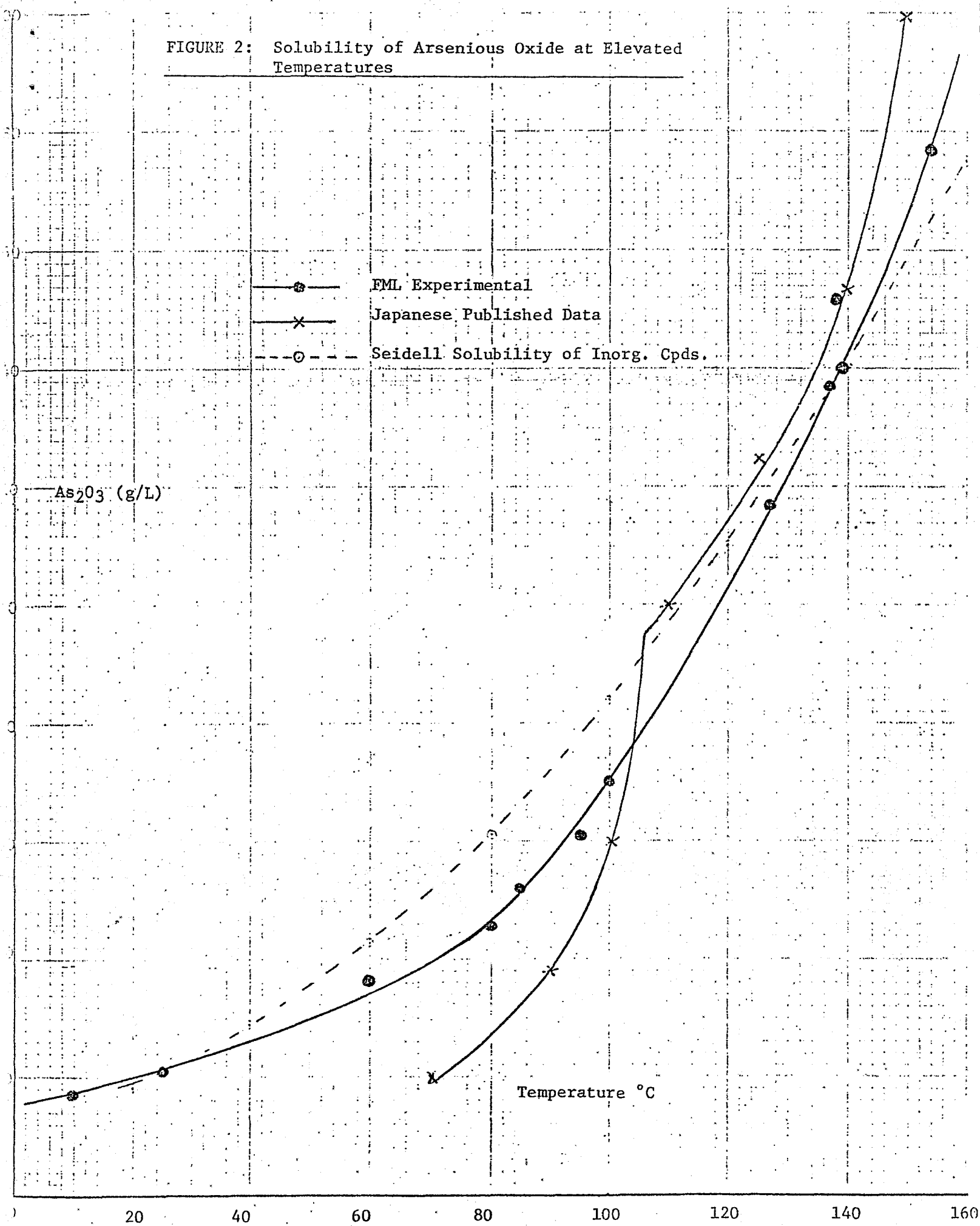


FIGURE 3: Incremental As_2O_3 Solubility as a Function of Temperature

$\Delta\text{As}_2\text{O}_3$ (g/L)

Temperature °C

