85-258 -14303

GEOLOGICAL BRANCH ASSESSMENT PEPOPT

REPORT ON BENEFICIATION TESTWORK ON GERMANIUM-BEARING CARBONACEOUS MATERIAL FROM THE KELLY 1 - 5 AND TRISH 1 - 2 MINERAL CLAIMS 05/86

> Located on Lang Creek, in the Vancouver Mining Division NTS 92 F/16 W British Columbia at 49° 48' N. Latitude 124° 25' W. Longitude

> > FILMED

Owned by FARGO OIL CORPORATION Operated by FARGO OIL CORPORATION and AMERICAN CYANAMID COMPANY

Gordon R. Hilchey, P.Eng. GORDON HILCHEY AND ASSOCIATES LTD. May 3, 1985

GERMANIUM-BEARING CARBONACEOUS MATERIAL FROM THE KELLY 1 – 5 AND TRISH 1 – 2 MINERAL CLAIMS

INDEX

		Page
1.0	INTRODUCTION	.1.
2.0	LIST OF CLAIMS	.2.
3.0	LOCATION	.2.
4.0	ACCESS	.3.
5.0	TOPOGRAPHY	.3.
6.0	HISTORY	.3.
7.0	GEOLOGY	.4.
8.0	FLOTATION TEST WORK	.5.
9.0	SIROSMELT RESEARCH	.7.
10.0	CONCLUSIONS	.8.
	ITEMIZED STATEMENT OF COSTS	.9.
	CERTIFICATE	.10.

ILLUSTRATIONS

PROPERTY LOCATION MAP CLAIM MAP Sample locations Follows page 1 Follows page 1 Pocket

APPENDICES

APPENDIX I	BENEFICIATION OF CARBONACEOUS GERMANIUM ORE
APPENDIX II	SMELTING OPPORTUNITIES WITH SIROSMELT TECHNOLOGY
APPENDIX III	RECOVERY OF GERMANIUM FROM FARGO COAL CONCENTRATES
	BY SIROSMELT FUMING

I. INTRODUCTION

Between 1981 and 1984 a germanium prospect located near Lang Bay, British Columbia, approximately 15 kilometres southeast of Powell River, was sampled a number of times by the writer on behalf of Fargo Oil Corporation. Analyses of the samples collected over the years, indicated an average germanium content of 70 ppm (70 grams/tonne).

As a result of the low germanium content of the crude ore, a series of mineral dressing and metallurgical steps will be necessary to upgrade the raw material to a marketable product. As previous attempts to upgrade the crude ore had met with indifferent success, it was judged that feasible methods of concentrating and upgrading the ore should be determined before embarking on an expensive exploration program to prove up ore reserves. Research over the past two years has resulted in establishing two satisfactory procedures to accomplish this.

During 1983, American Cyanamid Company conducted flotation test work on Lang Bay ore at their Stamford, Connecticut laboratory. The use of their proprietary reagents developed for flotation of oxidized coals proved successful. The suitability of their reagents and procedures were later confirmed at the laboratory of Bacon, Donaldson & Associates Ltd. of Vancouver.

On the recommendation of Dr. G. M. Swinkels, a consultant to Fargo, arrangements were made to evaluate the Sirosmelt process for further upgrading the Lang Bay flotation concentrate. Sirosmelt is a pyro-metallurgical process developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO) of Melbourne, Australia. Sirosmelt has features which appeared to be particularly suitable for upgrading the Lang Creek concentrate.

During April 1984, the author supervised the collection of a bulk sample for the CSIRO test work. The bulk sample was shipped to Cyanamid for

.1.





FARGO OIL CORPORATION

LANG BAY GERMANIUM/GALLIUM PROPERTY VANCOUVER MINING DIVISION Powell River, British Columbia

Claim Map

concentration and the concentrate was then shipped to CSIRO. The CSIRO test proved to be highly satisfactory. This report summarizes the results of both Cyanamid and CSIRO test work and recommends an exploration program.

2. LIST OF CLAIMS

Examination of mineral titles registered with the British Columbia Department of Mines and Petroleum Resources indicates the existence of the following mineral claims covering the area of the Lang Bay prospect near Powell River, B.C.:

Claim Name	Record Number	Number of Units	Expiry Date
Trish 1	873	20	May 4, 1985
Trish 2	874	20	May 4, 1985
Kelly 1	87 <i>5</i>	04	May 4, 1985
Kelly 2	889	20	May 8, 1985
Kelly 3	876	06	May 4, 1985
Kelly 4	877	20	May 4, 1985
Kelly 5	890	10	May 8, 1985
Zoie 1	1127	06	Dec. 15, 1985
Ryan 1	1687	04	Aug. 20, 1985
Ryan 2	1688	02	Aug. 20, 1985
Ryan 3	1699	06	Aug. 20, 1985

In summary there are 11 claims consisting of 118 units all owned by Fargo Oil Corporation. This report pertains to the Trish 1-2 and Kelly 1-5 mineral claims, known as the Kelly group.

3. LOCATION

The claim group lies 15 km southeast of the town of Powell River, B.C. and centered on Lang Creek. General boundaries are Malaspina Strait between Lang Bay and Myrtle Point to the south, Myrtle Creek and Hammill Lake to the west and northwest, Lang Creek to the north, and Whittall Creek to the east. The approximate coordinates are 49° 48' N and 124° 25' W. The NTS map reference for the area is 92F/16W.

4. ACCESS

Highway 101 follows the coast from Saltery Bay to Powell River and passes very near to the southern border of the Kelly claim group. A good paved secondary road connecting to Highway 101 between Lang Creek and Kelly Creek extends north and then west where a tote road in fairly good condition gives access to the outcrop area where the sampling was undertaken.

5. CLIMATE, TOPOGRAPHY AND LOCAL RESOURCES

The gently rolling terrain is gently sloping with a maximum elevation of approximately two hundred and fifty metres above sea level in the northeast corner of the property. The ground slopes down in a gentle fashion towards Malaspina Strait to the south. Lang Creek has cut its valley about fifteen to thirty metres below the general level of the surrounding area.

The area has a thick second growth of timber consisting mainly of fir, hemlock, and cedar with alder found along the stream banks.

The water supply is plentiful due to the many streams on the property, the main ones being centrally located Lang Creek and Kelly Creek, both flowing southeasterly and, to the west, Deighton Creek flowing southerly into Malaspina Strait. A high voltage power line passes across the property.

The climate is mild with an annual rainfall from 1000 to 1250 millimetres with minimal snowfall during the winter.

6. HISTORY

In 1948 a spectrographic research study on the coals of British Columbia discovered high values of germanium in the carbonaceous material found in the Lang Creek area. In 1957 the mineral rights to the area were acquired by the now defunct Taiga Mines Ltd. who carried out a trenching and drilling program during 1958 and 1959. In 1981 the property was acquired by the current owner, Fargo Oil Corporation who have conducted a total of 11 trenching and sampling programs between August 1981 and April 1984. Most of the recent work has consisted of research on methods of recovering germanium from the ore. Much of the research has been done by American Cyanamid Company, Stamford, Connecticut, who have conducted flotation tests, and CSIRO who have conducted pyro-metallurgical reserach.

7. GEOLOGY

The following description of the geology of the area of interest was prepared by the author and included in a pre-feasibility study on the Lang Bay property prepared by Wright Engineers Limited of Vancouver, British Columbia, dated November, 1983:

The property is underlain by a basin of thin-bedded Eocene sedimentary rocks composed of poorly to well consolidated shale, sandstone, arkose and conglomerate. The basin is about six km long and about four km wide. Observed dips are gentle (up to about 15° or 20°) towards the axis of the basin which trends northwest. The total thickness of the formation in the center of the basin is estimated to be about 450 metres. The sedimentary series is underlain by pre-Tertiary granitic rocks of the Coast Range and possibly other Mesozoic or earlier formations.

Arkosic rocks near the base of the formation and the underlying granitic rocks have been subject to weathering which has altered the feldspars to clay minerals and deposited small amounts of carbonate (mainly calcite) and pyrite. The weathering process was probably accomplished by ground waters under mainly reducing conditions although a few lenses of sandy sediments with red oxides of iron have been observed. Neither the time of the alteration or its relationship to the germanium mineralization, if any, is known.

Thin, discontinuous lenses of coal occur throughout the formation in both sandstone and shale members. The coal is probably the result of coalification of logs, branches and twigs scattered in the formation. This coal has always yielded significant values in germanium whenever it has been assayed. Where observed, however, the percentage of coal in this type of occurrence has always been very low.

Near the base of the formation along the northern rim of the basin, coal has been found in a dark brown horizon locally called a brown bed. The brown bed has an observed thickness of 0.5 to about five metres. Most of the coal in the brown bed occurs as discontinuous lenses 2 to 10 mm thick with an aggregate content of two to three percent coal. On the basis of the best data available the germanium content of the brown bed in Area 1 is expected to average 70 grams per tonne or better. The brown bed has been observed in four apparently distinct deposits but the lateral extent is not known. While most of the brown beds observed to date occur within a few metres of the weathered basement rocks, they are also known to occur higher in the formation.

In 1959 the brown bed was exposed for 60 metres along the south side of Lang creek in the central part of the property. It pinched out to the southeast but the limit was not found to the northwest along strike or down dip to the southwest.

8. FLOTATION TEST WORK

In April 1984 the writer supervised the collection of approximately one tonne of brown bed material from two locations on the Kelly group of claims. Approximately two hundred and seventy kilograms were forwarded to American Cyanamid in order to produce sufficient germanium concentrate to carry out testwork at CSIRO, Australia.

Before shipment to Cyanamid the samples were analysed by Chemex Labs. Ltd., North Vancouver, B.C. and were found to contain a minimum of 70 ppm germanium.

The flotation test work was fairly conventional and included investigation of the following variables:

- (a) size of feed, including desliming;
- (b) slurry density of feed;
- (c) type of conditioner and conditioning time; and
- (d) type of frother and flotation time.

Some of the important features noted by Cyanamid were:

(a) The amount of oxidation of the coal varied between samples. This was probably due in part to the depth below the outcrop from which

the samples were taken. Cyanamid's proprietary reagents appeared to be satisfactory for flotation of the oxidized coal although better results were always obtained on the less oxidized material.

- (b) Some samples had oxidized significantly while in storage, which indicates that care must be taken to prevent or limit oxidation between the time the samples are taken and the time the ore is floated. Furthermore, when production is achieved, stockpiling of ore must be kept to a minimum.
- (c) It was relatively easy to recover a good grade of concentrate from the coarser coal, but very finely divided coal resulted in a very dirty concentrate.
- (d) The coarser coal has the highest germanium content but there is considerable variation in the germanium content of the coarse coal between sample sites. Lesser amounts of germanium occur in the finer coals and, apparently, also in the silicate material.

Overall, the concentration of the germanium-bearing coal by flotation has been successful in upgrading a brown-bed feed containing 70 or 80 ppm germanium to a concentrate ranging from 1000 to 2200 ppm germanium – a ratio of concentration of about 15:1 to 30:1.

Cyanamid later upgraded about two hundred and seventy kilograms of brown-bed material by a combination of heavy media concentration and flotation to 2310 grams of concentrate for shipment to CSIRO for further testing in the Sirosmelt test furnace.

Cyanamid's report, "Beneficiation of Carbonaceous Germanium Ore", dated April 1985, is attached as Appendix 1.

9. SIROSMELT RESEARCH

During October 1984 a test program was carried out by CSIRO, Melbourne, Australia, utilizing the Sirosmelt process as developed by CSIRO, on the germanium concentrates prepared by American Cyanamid. As CSIRO has not invoiced Fargo Oil Corporation as yet, the work of CSIRO will not be included as assessment work for the year ending May 4, 1985 but will be included as assessment work for the year ended May 4, 1986.

Sirosmelt is a pyro-metallurgical technique developed by CSIRO during the early 1970's which has a number of unique features. Of particular interest to Fargo Oil are the following:

- (a) about 99% of the germanium in the coal concentrate reported in the fume (flue gases) which can be readily recovered with standard equipment;
- (b) the concentration ratio was about 20 or 30:1, yielding a product containing more than 3% germanium;
- (c) fine-grained feeds can be fed wet into the furnace;
- (d) the Sirosmelt furnace is suitable for small-scale operations;
- (e) the Sirosmelt furnace can be operated on a continuous basis.

Sirosmelt is a proven pyro-metallurgical technique with adequate computer support for optimization and control. A copy of the paper, "Smelting Opportunities With Sirosmelt Technology", which gives an overview of the process and its applications is included with this report as Appendix 2. CSIRO's report on the test work on the Lang Bay concentrate is included with this report at Appendix 3.

Further research on larger samples will be required to optimize the process for the Lang Bay ore.

10. CONCLUSIONS

Major upgrading of the crude germanium ore from Fargo Oil's Lang Bay property is feasible by first concentrating by froth flotation and then upgrading the flotation concentrate using Sirosmelt technology. The Sirosmelt fume has a content of approximately 3% germanium versus a raw ore content of about 70 ppm or 0.007% germanium. Further research will be required to optimize the flotation and Sirosmelt processes and also to produce a final marketable germanium product.

Considering the favourable results outlined above, it is recommended that an exploration program be undertaken to prove up reserves. A phased drilling program is recommended as described in detail in a report by the author dated November 16, 1983, which was included in the Pre-Feasibility Report of Wright Engineers dated November, 1983. The first phase is estimated to cost \$525,000.

Core samples recovered from this program should be forwarded to American Cyanamid for optimization of their flotation procedure and the resulting concentrate forwarded to CSIRO for refinement of the Sirosmelt fuming procedure, as applied to the Lang Bay coal concentrates.

Respectfully submitted

Gordon R. Hilchey, P.Eng.

May 2, 1985

ITEMIZED STATEMENT OF COST INCURRED BY FARGO OIL CORPORATION AND AMERICAN CYANAMID COMPANY

Fargo Oil Corporation

-

1.	Professional Fees and Services	
	G. R. Hilchey, P.Eng.: Preparation of report	
	1½ days @ \$500.00	\$750.00
	G. M. Swenkels, Ph.D., P.Eng.: Professional Fees	

(2 days @ \$500/day)	\$ 1	1,000
Expenses	\$	109

American Cyanamid Company

		Days*	U.S.\$	
1.	Grinding studies, flotation test			
	and heavy-media separations	14	9,800	
2.	Analytical Services	3.5	2,450	
3.	Consulting visit to Reno by P.V.			
	Avotins and A. Day (June 10 - 12/84)			
	Time	6	4,200	
	Transportation (\$1654 @ 20%)		331	
	Expenses		<u> </u>	
	Total		17,681	
	Exchange Rate (\$US) = \$1.30 Cdn. =			\$22,985
	Total			\$24,844

*1984 Standard Costs - US\$700 per day

CERTIFICATE OF QUALIFICATION

I, GORDON R. HILCHEY, of Suite 703, 850 West Hastings Street, Vancouver, British Columbia, Canada, certify:

- 1. THAT I graduated from the University of British Columbia in 1942 with the degree of Bachelor of Applied Science (geological engineering).
- 2. THAT I graduated from the University of Alaska in 1947 with the degree of Bachelor of Mining Engineering (mining).
- 3. THAT I am a registered professional engineer in the Province of British Columbia and the Yukon Territory.
- 4. THAT I have practiced my profession as a geological and mining engineer for more than thirty years.
- 5. THAT I supervised exploration work on the deposit which is the subject of this report in 1959 and supervised various sampling programs on the property from August 1981 to April 1984.
- 6. THAT I have no interest, direct or indirect, in the property which is the subject of this report, nor do I expect to receive any.

DATED at Vancouver, British Columbia this the <u>3rd</u> day of May, 1985.

Gordon R. Hilchey, P.Eng

APPENDIX I

 \int

BENEFICIATION OF CARBONACEOUS GERMANIUM ORE



BENEFICIATION OF CARBONACEOUS GERMANIUM ORE FROM LANG BAY

	Da	uys* US\$
Grinding studies, flotation tests a media separations	nd heavy-]	.4 9800
Analytical Services	3	3.5 2450
Consulting visit to Reno by P.V. Av A. Day (June 10 to 12, 1984)	otins and	
Time Trans Expen	portation ses	6 4200 1654 900
	TOTAL	\$19,004

* 1984 Standard Costs - US\$700 per day

Beneficiation of Carbonaceous Germanium Ore (from Lang Bay property, Fargo Oil Corporation)

10 kg. of Lang Bay ore, collected 4/83, were received at Cyanamid's laboratories in June 1983. The Ge in the ore was reportedly concentrated in the coal, which constituted only a few percent of the ore. Average Ge concentration in this original ore was 70 ppm (70 gm/ton). To make a second stage of recovery practical, it was necessary to first increase this concentration by a factor of at least 20, to 1500 ppm or higher.

We were informed that the coal was difficult to float by conventional methods. Since the coal was dispersed throught the clayey matrix as generally small pieces, it seemed likely that this coal was rather oxidized. Therefore, we investigated flotation of the coal using reagents we had developed specifically for floation of oxidized coals.

At Stamford, float tests were done first with a small glass cell (250ml capacity), then using a Denver flotation machine with a 1.1 liter cell. When useful flotation conditions were established, a visit was made to Bacon, Donaldson & Associates, Vancouver, where they were equipped with Agitaire cells. Work was concentrated on two reagents which we had found to be effective in flotation of more conventional oxidized coals. Of primary interest and importance are several results which confirm that desired high grades and good recoveries can be achieved with our process.

In the best test at Bacon, Donaldson & Associates, 71.6% of the Ge was recovered at a grade of 2190 ppm Ge in a concentrate that represented only 2.25 wt.% of the starting ore (20% solids, 0.47 kg/T coal promoter S-5707, conditioned 5 minutes, floated for 8 minutes with Aerofroth 88):

	wt.8	ppm Ge	% of Ge
Concentrate	2.25	2190	71.6
Tailings	70.3	20	20.4
Fines	27.4	20	8.0

At Stamford, our flotation tests were monitored for coal recovery, and specific analyses for Ge were not generally done. The two of our tests that were analyzed for Ge, however, gave results very similar to that above. For a flotation done in a

Denver cell (9% solids, 0.50 kg/T S-5708, conditioned 5 minutes, floated 5 minutes with Aerofroth 88), with the fractions sent to Bacon, Donaldson for analyses, results were:

	wt.8	ppm Ge	% of Ge
Concentrate	3.85	1420	78.1
Tailings	67.6	10	9.7
Fines	28.6	30	12.3

A still earlier flotation in our small glass cell gave 79.5% Ge recovery from the 28x325 mesh feed that went to the float cell (18% solids, 1.0 kg/T S-5707, conditioned 5 minutes, floated 5 minutes with Aerofroth 88):

	wt.8	ppm Ge	% of Ge
Concentrate	3.74	1750	79.5
Tailings	96.3	18	20.5

Ge in the fines was not measured at the time, but assuming losses in fines similar to above, overall Ge recovery was approximately 70%.

At least ten other floats with similar coal recoveries reinforce the conclusion that recoveries in this range of 70-78% are readily attainable, with corresponding concentrate grades of approximately 1500-2000 ppm Ge.

Recoveries of 70-78% mentioned above were all obtained with desliming (removal of -400 or -500 mesh "fines") prior to flotation. Without desliming, we consistently obtained lower grades and generally lower recoveries. For the best of such tests that was run at Bacon, Donaldson & Associates, 60.8% of the Ge was recovered at a concentrate grade of 1320 ppm Ge (20% solids, 0.50 kg/T S-5707, 5 minutes conditioning, floated 8 minutes with Aerofroth 88).

	wt.8	ppm Ge	% of Ge
Concentrate	3.40	1320	60.8
Tailings	96.6	30	39.2

On this original batch of ore, our processing gave good Ge beneficiation, as noted above, using a rather simple process, with these main steeps: 1) crush and attrition the raw ore to -28 mesh size (80+% of the ore breaks up to this size just by slurrying in water); 2) deslime (with hydrocyclone?) to remove fine clay; 3) condition slurry for 5 minutes with 0.5 kg/T coal promoter S-5707; 4) float, using an alcohol frother, for 5 minutes. Although satisfactory results were obtained with this process, many parameters have not necessarily been optimized; e.g. grinding, solids level, promoter dosage and composition, conditioning time, type and dosage of frother.

Several months after this original work, we examined several different Lang Bay ore samples, in attempts to generate a relatively large (approximately 2 kg) sample of high grade concentrate for studies on the next stage of concentration (fuming at CSIRO). These later ore samples were all of poorer quality than our original sample. In some cases the overall head grade was considerably lower; in all cases, the Ge was less concentrated in the coal fraction, making the maximum attainable grade lower. The coal fractions in these samples were also generally more oxidized (all of the samples apparently came from very close to the surface), leading to poorer recoveries.

It was found useful to isolate samples of the pure coal in the ore, using heavy media separation, in order to determine the Ge content in the coal itself. Since all of our work, as well as that of earlier workers, has indicated that essentially all of the Ge is in the coal, the Ge content in the isolated coal would determine the maximum possible grade for the particular ore sample. This grade varied considerably for the ore samples we evaluated, ranging from 1100 to 4200 ppm Ge in the coals. Grades for various isolated coals and flotation concentrates are given in the table below.

Ore sample	Concentrate	ppm Ge	Ge in ash
4/83, 70ppm Ge (3.1% coal)	Pure coal(+28m) Float (28x400m)	4200 1400-2200	5.2% 2000-3500ppm
12/83, 15ppm Ge	Float (28x400m)	270	
2/84, 30ppm Ge	Float (28x400m)	500	
4/84 North cut, 80ppm Ge (4.6% coal)	Pure coal(+28m) Coal(28x100m) Float (28x500m)	2700 2100 920-1020	3.4% 2.6% 2400-3000ppm
4/84 Pit #2, 80ppm Ge (12.3% coal)	Pure coal(+28m)	1100	1.4%

The samples of pure coal, which contained consistently just 8.0% ash, were obtained by heavy media separation, using either carbon tetrachloride or chloroform (1.59-1.56 gm/ml). Flotation concentrates were obtained as in earlier examples, using 0.5 kg/T S-5707 as coal promoter.

These later ore samples not only contained less Ge in the pure coals, but more of the Ge was in the fine (-400 mesh) fraction, up to 20% or more. Also, not only were the more recent ores more oxidized and difficult to float, but some of the original 4/83 ore had also clearly become more oxidized upon storage and flotation recoveries were considerably poorer. For all of these reasons, it is likely that the optimized process will include more grinding. Grinding will expose fresh surfaces, improving flotation recovery of the coal, as well as recovery from the fine fraction.

It became apparent that, in any given ore sample, only the coarser coal had the highest Ge content. Using the overall coal and Ge contents, calculated average Ge concentrations in the coals are only 1/2 to 2/3 or the values determined from the isolated coarse coals; e.g., the 4/84 ore with 3.1% coal and 70ppm Ge averages 2260ppm Ge in the coal; similarly, the 4/84 North cut ore with 4.6% coal and 80ppm Ge averages 1740ppm Ge in the coal. These averages are to be compared to 4200ppm and 2700ppm, respectively, for the isolated coarse coal fractions. It is not surprising therefore, that the best floation concentrate grades we achieve are approximately half of the corresponding coarse coal concentrations.

Because of the above problems with the ore samples available to us, we could not make a high grade (ca. 1500ppm Ge) flotation concentrate directly. We elected instead to make a composite, from coal separated by heavy media and flotation concentrates, with overall properties typical of what we would ultimately expect to produce, namely, about 1500ppm Ge and 25-30% ash. The following samples were sent to Fargo Oil Corporation on 6/1/84:

		ppm Ge	% ash	Ge in ash
Α.	540gm North cut coal	2700	8.0	3.38%
в.	870gm Pit #2 coal	1100	7.8	1.40
c.	900gm flotation concentrate	710	47.7	1490ppm
Tota	al 2310gm	1320	23.4	5640ppm

The coal samples were obtained from heavy media separations. Samples A, B and C were packaged separately, with the suggestion that they be all combined to give a composite with properties close to what we expect our eventual flotation concentrates to be.

A point indicated by the above table is that Ge concentrations can be increased by a factor of two or more simply by ashing (oxidizing the coal at 500-750°C). For a flotation concentrate with 25-50% ash, this would represent a 2 to 4 fold increase. These higher concentrations are probably what should be used when referring to a subsequent fuming process; whether the ashing is done as a separate step or happens naturally as a first stage of fuming, the inorganic ash residue is all that must be heated to the high fuming temperatures.

In summary, we have demonstrated a feasible process for flotation concentration of Ge in the Lang Bay ores, using our oxidized coal collector. As indicated above, more work needs to be done to optimize processing parameters, but we first need a large quantity of.ore that is representative of the entire deposit.

APPENDIX II

-

......

1

.

1

-

....

SMELTING OPPORTUNITEIS WITH SIROSMELT TECHNOLOGY

SMELTING OPPORTUNITIES WITH SIROSMELT TECHNOLOGY

J.M. FLOYD, Extractive Metallurgy Research Group Chemical Engineering Department University of Melbourne Parkville, Vic 3052

and

B.W. LIGHTFOOT, Ausmelt Pty Limited P.O. Box 117 Upper Beaconsfield, Vic 3808

Paper to the 113th AIME Annual Meeting Los Angeles, February 26 to March 1, 1984

SMELTING OPPORTUNITIES WITH SIROSMELT TECHNOLOGY

J.M. FLOYD and B.W. LIGHTFOOT

ABSTRACT

Submerged injection Sirosmelt technology provides new opportunities for smelting both sulphide and oxide feed materials. The flexibility of the Sirosmelt system allows a number of operations to be carried out in a single furnace. Together with the very high specific smelting rate achievable with the lance stirred system and its simplicity, this provides a new type of smelter which may operate effectively at much smaller capacities than alternative smelting systems. The capability of the system to handle a wide range of feed types with almost any fuel is also attractive for large scale smelting operations. Potential applications will be discussed in relation to the characteristics of the smelting system.

INTRODUCTION

The Sirosmelt submerged lancing furnace system was developed by CSIRO in collaboration with a number of Australian companies during the 1970s. A small scale pilot plant in CSIRO was used to develop the technology and investigate applications in the area of slag treatment.⁽¹⁾ This lead to industrial involvement in larger pilot plants on smelter sites at Associated Tin Smelters, E R & S, Copper Refineries and Mount Isa Mines. ^(2, 3) Trials of the Matte Fuming Process for recovery of Tin from sulphide materials were carried out in the CSIRO pilot plant⁽⁴⁾, and this demonstrated that the system could be used for sulphide smelting and lead to development of processes for smelting of copper⁽⁵⁾, lead⁽⁶⁾ and nickel concentrates.

Semi-commercial plants are being operated for tin smelting, tin slag reduction and for lead concentrate smelting. The largest plant built so far has a smelting capacity of 5 tonnes per hour (tph) and larger scale developments will involve larger lances and multiple-lance furnaces. Neither of these aspects are considered to involve unexpected difficulties. Scale up of lances from the 50 kg pilot plant with 25 mm lances in CSIRO to the 4 tph matte fuming pilot plant with 125 mm lances operated by Aberfoyle Limited at Kalgoorlie was quite straightforward. The first one tonne pilot plant incorporated the use of multiple lances.

Larger scale development of major smelting plants for lead, copper and nickel smelting offers a number of potential advantages over alternative smelting processes for specific situations and work is proceeding towards larger plants. There are smelting opportunities which are opened up by the successful operation of plants up to smelting rates of 10 tph, and the application to smaller plants can be considered as employing "proven technology". It is the aim of this paper to stimulate consideration of the use of Sirosmelt technology for bringing on stream operations on small deposits which are not amenable to economic exploitation using conventional technology. The areas where Sirosmelt could be considered now are for:

- 1. small scale production
- 2. complex materials
- 3. oxides as well as sulphides requiring treatment
- 4. direct smelting of ore
- 5. secondary feeds, such as scrap, fume, slag, dross etc.
- pilot investigations for process route developments in a realistic smelting system operable on a small scale

Some specific applications are listed in Table 1. Examples of sulphide smelting and oxide smelting opportunities are described later.

THE SIROSMELT FURNACE SYSTEM

The Sirosmelt furnace system can be considered in its four main components:

- the furnace feeding (material handling and feed rate control)
- the Sirosmelt reactor system (refractory-lined vessel, flue off take and lance system)

3. the tapping and liquid product handling system

4. the flue gas system

The components of a Sirosmelt furnace system are shown in Figure 1. The feeding, liquid product handling and flue gas systems are all moreor-less conventional and there are a range of possible approaches to design. They will not be considered in detail here, although the unique features of operation of the Sirosmelt reactor allow unconventional approaches to be used for feeding, and significant developments in simplifying the feeding system are possible. For example fine feed can be lightly agglomerated by wetting, or can be fed dry down the lance using an injector.

Details of the reactor system are shown in Figure 2. The refractorylined vessel would normally be stationary for small-scale operations, but where very short cycle-times for batch treatments are involved, such as in copper converter slag reduction, a tilting furnace on trunnions would be employed. The flue off-take acts as an after burner in many applications and for this reason it is often refractory-lined, but designs incorporating cooled steel off-takes are appropriate for some applications.

The vessel may be refractory-lined and insulated for applications where heat losses must be limited and refractory life is acceptable. Where very aggressive slags or high temperatures are employed, water cooling is required behind refractories to ensure long campaigns between vessel relines.

The heart of the reactor is the Sirosmelt lance. This is nonconsumable and constructed of mild steel pipe. Air blown into the furnace cools the outer steel pipe and by the manner of operation of the lance it is coated by solid slag before immersion into the bath.⁽⁷⁾ The solid slag layer protects the steel from attack by the liquid slag bath.

Injected gas from the lance creates a cascade of slag above the surface in rising through the slag layer. The lance effectively pumps slag from the lance tip through the top surface. For a central lance operating in a cylindrical vessel, there is a relatively quiescent region beneath the lance. Droplets of slag are ejected into the gas space above the cascading bath and for this reason a high freeboard is provided to contain splashed slag within the vessel. Simple guides provide support and control of the lance position during raising and lowering by hoist.

Oxygen enrichment of process air to high oxygen levels can be achieved, but pure oxygen smelting is not possible with the simple air cooled lances. Water or oil cooled lances can be designed for use with pure oxygen. Fuel and fine materials are conveyed down the lance through inner tubes, which are used to support the swirlers.

Coarse materials are dropped into the furnace through a feeding chute and are rapidly incorporated into the bath on the cascading slag surface.

The system may be operated with continuous feeding and a constant bath volume maintained by continuous tapping. Alternatively the feeding can be interrupted to remove products during a tapping or pouring operation, leaving a heel of slag in the vessel to initiate the following feeding cycle.

Where separation of phases into two layers is difficult or slow, as in the case of copper matte settling from slag, it is necessary to provide either a quiescent period before tapping, by raising the lance, or a settling forehearth external to the Sirosmelt reactor.

CHARACTERISTICS OF SMELTING WITH THE SIROSMELT SYSTEM

The conditions in the Sirosmelt reactor are unique amongst furnace systems. Sirosmelt operations are characterised by the following features.

1. Very high smelting rates. Smelting rates of sulphide and oxide material as high as 1 tonne per cubic metre of vessel volume per hour have been achieved. This is an order of magnitude greater than conventional furnaces, such as reverberatory or electric furnaces, and the system can be considered in the category of the new "intense" smelting systems, such as TBRC and cyclone smelting furnaces. The rate of smelting is ultimately limited by the capacity of the bath to accept unsmelted charge. An increase in effective viscosity of the liquid-solid mixture causes a decrease in heat transfer

from the combustion gases or a decrease in utilisation of injected smelting air.

The high smelting rate results in the system being fuelefficient down to quite small smelting capacities. The system is manageable at smelting rates down to 50 kg per hour and it is fuel efficient at rates of 0.5 to 1 tph. The small plant size resulting from the high specific smelting rate allows ease of control of low-level emissions around the plant by the use of suitable venting systems.

2. The conditions in the furnace bath can be controlled accurately and rapidly changed by changing the injection conditions or by making additions of reactants. The bath can be rapidly oxidized by injecting air, or oxidizing air-fuel mixtures. Reduction of the bath can be rapidly achieved by injection of slightly fuel-rich fuel-air mixtures and at the same time feeding lump coal. Sulphidizing reagents can be added to form a matte phase or to fume off volatile sulphides. The temperature can be rapidly changed by injecting more or less fuel and air through the lance. The slag composition can be rapidly altered by adding fluxes.

In general the conditions in the furnace can be changed within minutes. This results in a very flexible smelting unit with the ability to carry out a number of sequential chemical operations in a single furnace without the need to tap products. This flexibility allows the Sirosmelt system to make

separations between a number of valuable components in a feed, so that complex feed materials can be smelted to produce different saleable products. For example a tantalum - tin - copper ore or concentrate could be smelted to give high recoveries of the three values to a tantalumrich slag, a tin-rich fume and a copper-rich matte. The same Sirosmelt system could also be used for upgrading the copper matte to blister or anode copper, and the tin fume to crude tin metal.

The capability of the system changing the conditions in the bath rapidly in response to changes of process variables entails the requirement that the feeds to the furnace and lance must be under good control. Techniques are also required to determine the furnace conditions in terms of the variables employed.

3. The ability of the Sirosmelt system to accept almost any form of feed material and smelt it efficiently provides opportunities for provision of a very simple feeding system. The system will accept lump-ore to sizes up to approximately 50 mm, so that mining and coarse crushing may be the only pre-treatments required. The system will also accept wet feed without problems, so that drying of feed is not required by the process. Fine material can be injected down the lance. If added at the charging chute, fine material will blow out of the furnace in flue gases, so that wetting or a light agglomeration of fine feed to the furnace is required to ensure incorporation in the bath.

- 4. The vessel is simple and cheap to construct so that the capital cost of a small plant is not excessive in relation to its capacity provided a simple feeding and gas handling system is practicable.
- 5. The smelting system is robust in that the furnace and equipment is capable of withstanding considerable physical, chemical and thermal abuse without failing. Damage can be quickly and cheaply repaired if it does occur, and does not result in extensive down time. The lance system can be operated to remelt a solidified bath, as an example, so that highly skilled operators are not essential.

SMALL-SCALE APPLICATIONS FOR SULPHIDE SMELTING

Small-scale copper concentrate smelting involving sequential operations of smelting, conversion to white metal and conversion to blister copper in a single furnace was described previously following small pilot plant trials.⁽⁵⁾ The flowsheet for this operation is shown in Figure 3. Single furnace operation in the Sirosmelt system will result in relatively low capital, labour and fuel requirements. A plant producing an upgraded material in a remote location would not necessarily entail higher smelting costs than a large smelter accepting concentrate for toll smelting.

The ability of the Sirosmelt system to efficiently smelt oxidized or low sulphur material which cannot be accepted by conventional smelters could increase the revenue available from an ore body by allowing smelting of weathered material as well as the sulphide deposit.

Volatilisation of impurities in copper concentrates, such as zinc, tin, lead and arsenic, can be enhanced during the smelting stage by operation at optimal matte grade, temperature, and, where required, by modification of the oxygen potential by addition of coal during smelting. Thus impure copper concentrates can be effectively smelted to produce relatively clean blister copper. The fume may be saleable directly in the case of a high zinc, tin, or lead tenor, or can be further upgraded by smelting in the main Sirosmelt system or a subsidiary unit to yield a product of higher value if this is economically justified.

The matte phase acts as a collector for precious metals, so that recovery of these during smelting does not impose difficulties. Where the precious metals have a value which is comparable to the copper in the feed material, but the total tonnage of feed is too low to justify construction of a refinery, production of high grade matte for sale may be preferable to blister production. In this case the operation would be preferably carried out by continuous feeding and tapping of the furnace. The product from continuous tapping will be matte suspended in slag, and in order to achieve a discardable slag the continuous stream is discharged into a settling forehearth. The forehearth is tapped for slag at an overflow notch and for matte at a siphon taphole opened periodically.

SMALL-SCALE APPLICATIONS IN OXIDE SMELTING

Previous papers (1, 2) have outlined the use of the Sirosmelt system for tin slag reduction and tin concentrate smelting.⁽⁸⁾ These two

applications are being developed to commercialisation.

The matte fuming process (4, 9) was developed in collaboration by CSIRO and Aberfoyle Limited to a scale of 4 tph of feed. The application is at present being considered for commercialisation.

The recovery of copper nickel, and lead from smelter slags has also been investigated quite extensively. These applications are well documented. It is the aim of the present paper to illustrate new applications which have not been previously described in the literature and the work on slags⁽¹⁰⁾ will not be detailed here.

The recovery of zinc from slag dumps and silicate ores represents an interesting possible application of the Sirosmelt system. Small-scale crucible testwork has indicated that reduction and fuming of zinc from slags accomplished by feeding lump coal into the slag whilst injecting gases gives zinc removal rates which are not affected significantly by the slag basicity. Fuming rates quite similar to the zinc slag fuming process rates were achieved with both acid and basic slags.

The Sirosmelt system uses fuel more efficiently for smelting slag or silicate ore than the water jacketed slag fuming furnace. This is because the refractory lined Sirosmelt system minimises heat losses. The fuming furnace relies on cooling water to solidify a slag layer on the steel shell. This entails large heat losses through the thin slag layer, of relatively high thermal conductivity. The Sirosmelt process would produce a zinc fume, and this is an acceptable feed to an electrolytic zinc plant. Depending on the volatile impurity content of the feed material further processing of the fume may be required.

The Sirosmelt system may be operated to produce two separate fumes and so carry out an upgrading of the zinc fume. In order to separate volatile compounds such as lead, arsenic and bismuth from the zinc fume the initial smelting operation would be carried out under relatively oxidizing conditions to ensure that zinc reported to the slag, whilst the other volatile components reported to fume. Enhancement of the fuming of elements with a volatile sulphide, such as lead and tin, can be achieved by addition of iron sulphide containing materials during smelting. When the furnace capacity for slag was reached the temperature would be raised and feeding of lump coal initiated to fume zinc, which would be collected in a separate baghouse or precipitator system.

CONCLUSIONS

The Sirosmelt system provides a new type of reactor for carrying out smelting operations. The unique features of the system allow consideration of the commercial application of smelting processes to a wider range of feed materials than previously feasible. Possible small scale applications have been described in the smelting of ores and complex sulphide and oxide materials and many potential sources of metals in recycle materials whose commercial treatment in a separate circuit could now be considered. These include drosses, fumes and slags. There are many other smelting opportunities which are opened up by the Sirosmelt system. Evaluation of specific cases requires detailed information about particular potential feed materials.

REFERENCES

- J.M. Floyd, "The submerged smelting of tin slags A new approach to lower-grade concentrate smelting". Fourth World Conference on Tin, Kuala Lumpur, 1974. N.L. Phelps ed, Vol. 3, pages 179-190.
- J.M. Floyd, and D.S. Conochie "Reduction of liquid tin smelting slags 2 - Development of a submerged conbustion process". Trans IMM, <u>88</u>, Cl23-l28 (1979).
- 3. J.M. Floyd, G.J. Leahy, R.L. Player and D.J. Wright, "Submerged combustion technology applied to copper slag treatment". Aus IMM Conference, North Queensland, Sept. 1978, 323-337.
- K.A. Foo and J.M. Floyd "Development of the matte fuming process for recovery from sulphide materials". Lead-Zinc-Tin '80. Ed. J.M. Cigan, T.S. Mackey and T.J. O'Keefe 786-800 (1980).
- 5. J.M. Floyd, N.C. Groue and B.W. Lightfoot, "Small pilot plant trials of Sirosmelt copper smelting" Australia-Japan Extractive Metallurgy Symposium, Sydney, 1980. Aus. IMM, 63-74.
- W.T. Denholm, A.N. Parry, J.M. Floyd and W.J. Errington. 'High intensity lead smelting process". UK Patent No. GB 2113253A, 23 Nov. 1982.
- 7. J.M. Floyd "Submerged injection of gas into liquid pyrometallurgical bath". US Patent No. 4251271, 17 Feb. 1981.
- 8. J.M. Floyd "Recovery of tin from slags". US Patent No. 390 587, 16 Sept. 1975.
- 9. W.T. Denholm and K.A. Foo "Recovery of tin from ores or other materials". US Patent No. 4,274,868, June 23, 1981.
- 10. J.M. Floyd and P.J. Mackey, "Developments in the pyrometallurgical treatment of slags. A review of current technology and physical chemistry". Extractive Metallurgy '81, IMM, 1981, 345-371.

TABLE 1 : SMALL-SCALE APPLICATIONS

Sulphide Feeds

Copper smelting to blister copper in a single furnace Complex materials - e.g. copper with zinc and precious metals Lead - zinc ore

Pilot simulation of other smelting processes

Oxide Feeds

Tin slag reduction, tin smelting

Tin fuming as sulphide

Slag treatment (copper, nickel, lead)

Zinc fuming from slag or silicate ore and from complex oxides

Fume and dross smelting

Smelting weathered zones of sulphide copper, nickel, lead or zinc ores

FIG.1 COMPONENTS OF A SIROSMELT FURNACE SYSTEM





APPENDIX III

[]

57

RECOVERY OF GERMANIUM FROM FARGO COAL CONCENTRATES BY SIRSMELT FUMING Institute of Energy and Earth Resources

Division of Mineral Engineering

RECOVERY OF GERMANIUM FROM FARGO COAL CONCENTRATES BY SIROSMELT FUMING

W.T. Denholm, R.N. Taylor and S. Saunders

March 1985

Mineral Engineering Communication

RESTRICTED CIRCULATION This document is not to be given additional distribution or to be cited in other documents without the consent of the Division of Mineral Engineering.

Division of Mineral Engineering, P.O. Box 312, Clayton, Victoria 3168, Australia

MIE 60

RECOVERY OF GERMANIUM FROM FARGO COAL CONCENTRATES BY SIROSMELT FUMING

Γ

W.T. Denholm, R.N. Taylor and S. Saunders

.

March 1985

ASBSTRACT

122.79

Computer modelling of Sirosmelt fuming of a germanium-rich coal concentrate suggested that germanium recoveries in excess of 99% could be achieved. However with some of the samples supplied, a large excess of heat was available even when burning the concentrate in a slag bath under very fuel-rich conditions.

The results of the modelling studies were confirmed in a continuous cruciblescale test in which the coal was injected with a deficit of combustion-air through a miniature submerged-combustion lance. Germanium recovery of 99% was inferred from the slag analysis, and the fume contained 3.6% Ge.

Future test work and modelling are recommended, to optimize feed rate, flux additions and slag recycle.

1. INTRODUCTION

Some preliminary computer simulations of fuming operations for the recovery of Ge from flotation concentrates supplied by Fargo Oil Inc. were attempted using two packages available on CSIRO computer networks [1, 2].

The early work using the assays initially supplied in February 1984 was done using the CSIRO-NPL 'Thermodata' system. This is a universally applicable chemical equilibrium package which can be adapted to practical smelting operations by assuming an overall heat loss per unit of feed smelted.

More recently the simulations have been done using the 'SMELT' model which is capable of the same thermodynamic performance as 'Thermodata' but is specifically designed to simulate converter-type smelting operations such as Sirosmelt. Using this package the furnace heat losses are computed on-line from furnace design data entered in the model. Either batch or continuous tests can be simulated under conditions of automatic temperature control. The fuel rate is then automatically adjusted to maintain the bath temperature, while the flux rates are adjusted to maintain the slag composition at a preset value.

The results of the modelling were used to establish the conditions for crucible scale tests. Early simulations were done for a concentrate forwarded in February 1984. Later ones were done with three concentrate compositions denoted A, B and C in the text, while a successful submerged combustion fuming test was done on concentrate C [3].

The operating strategy proposed for "Sirosmelt" processing is to feed the dry powdered concentrate down a coal-burning lance, using its "coal" fraction as both fuel and reductant. Fluxes will be dropped into the vessel from above, using a suitable gravimetric belt feeder.

2. SIMULATED Ge FUMING

2.1 The Preliminary Concentrate

Starting conditions for the first Fargo concentrate were determined so the initial heat load would be as low as possible. Thus a minimum of flux addition to the feed material was chosen, that would give a maximum acceptable liquidus (1200°C).

The feed composition was based on assays supplied by Fargo Oil (February 1984) (Tables 1 and 2). Minor components, such as MgO, K_2^0 and TiO₂ were omitted for simplicity of thermodynamic calculations and because their effect on the liquidus at

- 1 -

this level will be small. The carbon, hydrogen, nitrogen and sulfur were assumed to be associated with a coal and were represented by a North American coal of similar C and S content and comparable content of volatiles. The coal chosen has the composition 76.6% C, 5.7% H, 0.9% N, 9.7% S, 7.1% O.

A prefluxed starting slag bath was prepared to closely resemble the expected final slag composition.

The quantities of FeS used were chosen on the basis of minimum sulfur requirement for tin fuming in a slag bath as described by V.G. Brovkin (U.K. Patent 1391572, April 1975), i.e. total sulfur in bath approximately 6%.

One criterion for successful fuming is that the reaction should require little extra heat input and preferably it should be autogenous. Experience has shown that the heat loss from a furnace operating at a feed rate of 4000 kg/hr would be about 370 M joule/hr. On this basis, for a small scale crucible test, a 50 K joule heat output is required from the smelting and combustion reactions when treating 300 g of Fargo concentrate to simulate an autogenous process. The effect of blowing varying amounts of air was simulated (see Table 3). It can be seen that about 75% of the stoichiometric air for complete combustion to CO_2 and H_2O results in acceptable Ge recovery as well as giving the required heat output for the concentrate under consideration (i.e. the first concentrate supplied in February 1984).

Varying the FeS additions (Tables 3 and 4) illustrated that successful Ge fuming can be achieved with no extra FeS, using only the sulfur in the feed.

The effect of replacing some of the "coal" with a typical fuel oil of composition 88.4% C, 11.3% H, 0.3% S was tried. The results (Table 4) indicate that satisfactory Ge fuming can also be attained in these cases.

2.2 Work on the Later Concentrates

قشين

Further simulations (and experiments) were carried out on samples supplied by American Cyanamid in June 1984.

Analyses of these samples are set out in Table 5. As before, the organic C, H and S were assumed to be associated with a coal, the formula of which was established by comparison with a North American coal of similar composition.

The criteria for calculation of flux requirements were to keep the Al_2O_3 content down to 10%, to minimise the viscosity and to keep the total flux addition as low as possible while achieving a liquidus under 1100°C (Tables 6A, B, C).

- 2 -

The starting slag was fluxed to resemble the expected final slag composition (Table 7). The weight of the starting slag bath was increased from 200 g to 500 g to ensure adequate mixing dynamics to assist with incorporation of fluxes and combustion of the hydrocarbon fraction.

Based on previous simulations no extra sulfur was added, and sufficient air was used to give 75% stoichiometric combustion to CO_2 and H_2O . The results of the latest simulations indicate that for all three samples, and for a mixture of the three, satisfactory Ge extraction should occur and the reaction would be autogenous (Table 8).

3. EXPERIMENTAL STUDIES

It was found that the usual feeding technique of adding pelletized feed materials (Fargo concentrate plus flux) into the air-agitated molten bath resulted in much of the coal burning above the bath rather than being incorporated and reacting within the bath. As a result the slag immediately became over-oxidized and overloaded with undigested solids, forming a pasty mass. This was remedied by sparging the partially burned Fargo concentrate into the bath, utilising a miniature concentric submerged-combustion lance in which the concentrate was blown with carrier gas down a central tube and combustion air was blown down the annulus. The experiment using this technique with Fargo concentrate 'C' was run to completion, and the lance performed very well as a submerged-combustion lance.

In the successful submerged combustion smelting test, a starting slag bath of 500 g of copper slag (Table 7) was melted in the weighed crucible assembly illustrated in Fig. 1. The coal concentrate was fed at the rate of 2.6 g/min from a miniature belt feeder and entrained in carrier gas. Air was blown through the annulus at the rate of 9.3 l/min, while fluxes were fed at a uniform rate in pelletised form during the blowing operation. Table 6C shows the total inputs of the components of feed and flux required for an addition of 250 g of concentrate. However, in the actual experiment, 233 g of concentrate was added with 41 g of flux, and the important results are shown in Tables 8 and 9.

Fume was cooled and collected in a miniature bag filter and at the end of the test the crucible was allowed to cool and solidify and was reweighed to determine the weight of slag. The fume and slag were assayed to determine the distribution of germanium.

The relevant parts of the material balance are given in Table 9. Unfortunately it is not possible to collect all fume in these experiments and the germanium recovery must be inferred from the slag analysis.

- 3 -

Much of the fume and dust were made up of concentrate coal and ash components, which must have blown out of the melt, together with heavy metals from the starting slag. The metal contents were: Fe 4.5%, Cu 2.6%, Zn 6.2%, Pb 2.5%, TiO_2 8%, CaO 14%, Al_2O_3 6.4%. The germanium content of the fume was encouragingly high at 3.6%.

In this test a large starting slag bath was used to ensure reasonable process dynamics on the crucible scale. In a practical process using a suitable refractory-lined vessel the slag would be tapped intermittently, leaving a heel of starting slag for the next cycle.

Table 8 shows that excessive heat would be generated when treating any of the concentrates, and it would be desirable to use iron ore as a source of iron for the fluxing operation, and to add a coolant such as recycled slag or perhaps water mist entrained in the combustion air.

4. CONCLUSION

-

- (a) Thermodynamic analysis shows the feasibility of fuming of germanium in a bathsmelting operation such as Sirosmelt, in which the Fargo coal concentrate is partly burned as fuel in a lance or tuyere. The model has been validated by a small scale experiment.
- (b) Excessive heat is generated by burning the concentrate, and it would be necessary to add large quantities of flux (preferably limestone and iron ore, which both involve endothermic reactions) to permit operation at high feed rate. Other methods of temperature control need to be investigated, for example recycle of granulated slag as coolant.

5. FUTURE WORK

(a) Modelling:

A set of files and a dedicated data set have been set up for simulation by the SMELT model of the fuming of germanium from Fargo concentrate in bath-smelting furnaces of various types. This system can now be employed to model variants of the process with the particular aim of optimising production rate, bearing in mind the excessive heat generation.

(b) Experimental Studies:

The single result reported here shows that the process chemistry can be tested on the small scale, and the results agree with model predictions. Further crucible-scale test work will be devoted to:

- 4 -

- (i) Optimization of flux additions to provide a suitable slag at the lowest cost from fluxes available near the proposed plant site.
- (ii) Maximization of production rate by a study of the conflicting effects of oxygen partial pressure (as set by air-to-concentrate ratio). Low oxygen partial pressure (i.e. high concentrate to air ratio) favours lower heat release and higher germanium recovery, each of which permit higher rate of addition of the concentrate which is also the fuel. However excessive reduction by carbon promotes iron precipitation which must be avoided.
- (iii) Following the small-scale work, the proposed process chemistry and operating strategy would be tested on the 50 kg pilot scale to provide information on scale-up.

There will be a close interaction between the modelling and experimental studies to provide the most cost-effective path to the data required for process design.

(c) It will also be necessary to optimize the overall 'ore-to-fume' process strategy including the flotation step and slag recycle since the composition of the concentrate has a large bearing on the heat balance of the smelting stage. Flow-sheeting packages are available in the Division to achieve this objective.

REFERENCES

-

Π

- Turnbull, A.G. and Wadsley, M.W. Thermodynamic modelling of metallurgical processes by the CSIRO SGTE thermodata system. The Aus.IMM Melbourne Branch Symposium on Extractive Metallurgy, November 1984, p.79.
- McClelland, R.A. and Denholm, W.T. A mathematical model of the Sirosmelt process. The Aust.IMM Melbourne Branch Symposium on Extractive Metallurgy, November 1984, p.95.
- Denholm, W.T. Small scale simulation of submerged-combustion smelting processes. Proc. MMIJ/Aust.IMM Joint Symposium, Sendai, Japan, 6-8 October 1983, p.165.

Table 1 Assay of Fargo Concentrate (February 1984)

Component	Assay (%)				
S	2.2				
с	17.4				
sio ₂	32.77				
Al ₂ O ₃	21.40				
Fe 203	5.2				
TiO2	1.5				
MgO	0.23				
CaO	1.3				
Na 20	0				
κ ₂ 0	0.3				
Loss on ign.	35.7				

,



1

 $\begin{bmatrix} 1 \end{bmatrix}$

.

-

*, **199**

.

[]

	Weight of Spe	terials (g)			
Species	Starting Slag	Feed	Flux		
	(Prefluxed)	(Fargo Cons.)	for 16% Al ₂ O ₃		
*Coal		67.4			
A1 20 3	32.0	64.2			
CaO [,]	26.0	3.9	48.3		
Cu ₂ O	3.2				
FeO	62.0				
Fe ₂ 03		15.6	122.7		
GeO2		0.45			
н ₂ о		43.8			
sio ₂	80.0	98.4	62.1		
Total	203.2	293.8	233.1		

Table 2Inputs to System (April 1984).Crucible Test Simulation+.

 $\pi^{*} \mu^{*} \xi_{\mu}$

Π

Γ

+ Simulating autogenous Sirosmelt operation at 4000 kg/hr.

* Coal was C_{6.377}, H_{5.655}, N_{0.064}, O_{0.444}, S_{0.303} representing the coal fraction of the concentrate. In some simulations, part of this species was replaced by fuel oil, C_{7.36}, H_{11.211}, S_{0.009}.

						Eq	uilibri	um		
•		I	nput	(g)		Di	stribut	ion	Enthalpy	Log
sto				·			Ge (%)			
500	0.	No	FeS	Fuel	Fargo	G	as	Slag	it jouro	P.º 2
	•2	"2			Cons*	GeO	GeS	Ge02		
90	153	507	0	0	293.8	26.7	0.91	72.4	-404	-7.61
90	153	507	3	0	293.8	31.7	2.9	65.4	-387	-7.85
90	153	507	6	0	293.8	35.1	7.5	57.4	-371	-8.60
80	136	451	0	0	293.8	17.7	72.0	10.2	-189	-9.03
80	136	451	3	0	293.8	14.3	77.9	7.8	-177	-9.09
80	136	451	6	0	293.8	11.8	82.1	6.1	-166	-9.14
75	128	423	0	0	293.8	9.1	87.1	3.7	-87	-9.37
75	128	423	2	0	293.8	8.1	88.6	3.2	-80	-9.39
75	128	423	4	0	293.8	7.3	89.8	2.7	-74	-9.41
70	120	394	ο	0	293.8	6.0	92.1	1.9	3	-9.62
70	120	394	2	0	293.8	5.4	92.9	1.7	9	-9.64
- 70	120	394	4	0	293.8	4.9	93.5	1.5	15	-9.66

Table 3 Effect of Varying Air and FeS Input on Ge Fuming

10

.

Π

Π

Sto = stoichiometry, i.e. theoretical air requirement to produce $CO_2 + H_2O$.

* February 1984 concentrate.

8		I	nput	(g)		Equ Dis	ilibri stribut Ge (%)	um ion	Enthalpy K joule	Log pO a
510	O ₂ N ₂ FeS Fu		Fuel	Fargo Cons*	Gas GeO GeS		Slag GeO ₂	K JULLU	F~2	
75	128	423	0	0	293.8	9.1	87.1	3.7	-87	-9.37
75	128	423	2	0	293.8	8.1	88.6	3.2	-80	-9.39
75	128	423	4	0	293.8	7.3	89.8	2.7	-74	-9.41
75	128	423	0	8.4	257.2	7.5	90.0	2.4	-82	-9.56
75	128	423	2	8.4	257.2	6.7	91.2	2.1	-76	-9.58
75	128	423	0	16.4	222.3	6.8	91.4	1.8	-76	-9.73
75	128	423	2	16.4	222.3	6.0	92.4	1.6	-70	-9.74

Table 4 Effect of Fuel Oil and FeS Additions on Ge Fuming

.

 $\left[\right]$

Ω

and the second

• February 1984 concentrate.

Components	Sample A	Sample B	Sample C	
FeO	3.69	0.090	0.43	
sio ₂	23.0	2.53	2.40	
Al ₂ O ₃	12.9	2.01	1.58	
CaO	1.74	1.82	1.23	
MgO	0.66	0.22	0.19	
TiO2	1.32	0.61	0.66	
Na ₂ 0	0.89	0.18	0.21	
к ₂ 0	0.42	0.053	0.053	
н ₂ 0	4.7	6.6	16.3	
Coal	46.3	82.5	76.0	
Ge	0.071	0.270	0.110	
S (inorg.)	0.62	0.46	0.24	

Table 5 Analyses of Fargo Concentrates (June 1984) on an "As Received" Basis (%)

_ -

Č2

Π

بر ج Sample A: Flotation cons - North Cut ore. Sample B: Germanium ore cons - North Cut ore. Sample C: Germanium ore cons - Pit 2.

Table 6A

Ģ []

.

Species	Fargo Conc. A	Flux
Al ₂ O ₃ CaCO ₃ CaSO ₄ Fe Fe ₂ O ₃ GeO ₂ H ₂ O SiO ₂ C5.87, H _{5.} 794, N _{0.103} , O _{1.369} , S _{0.01} Total	32.2 6.6 1.59 - 10.2 0.25 11.8 57.5 115.8	- 87.5 - 103.2 - - 66.5 - 257.2

Table 6B

Species	Fargo Conc. B	Flux
Al 203 CaC03 CaS04 Fe Fe 203 GeO2 H20 SiO2 C6.119, H4.762, N0.064, O1.28, S0.01	5.02 4.53 4.88 - 2.51 0.97 16.5 6.32 206.2	9.42

Table 6C

Species	Fargo Conc. C	Flux
Al ₂ O ₃ CaCO ₃ CaSO ₄ Fe Fe ₂ O ₃ GeO ₂ H ₂ O SiO ₂ C6.219, H _{4.861} , N _{0.064} , O _{1.198} , S _{0.011} Total	3.95 3.63 2.53 - 1.19 0.40 40.75 6.0 190.0	- 10.6 - 18.5 - - 15.2 - 44.3

.

1972

{

[]

 \Box

Table 7Composition of Starting Slag (September 1984)

Species	Weight (g)	95
Al ₂ 0 ₃	50.1	9.0
CaSiO ₃	185.6	36.4
Cu ₂ 0	9.8	1.9
FeO	185.3	36.3
sio ₂	79.1	15.5

		Inpu	t (g)	Eq Di	uilibri stribut Ge (%)	um ion	Enthalpy K joule	Log pO ₂
	0 ₂	N2	Fargo Coalt	Ga GeO	s GeS	Slag GeO ₂	k joure	
Simulation:								
A	185	609	115.8	15.8	82.9	1.3	-307	-10.54
В	330	1088	206.2	15.4	83.8	0.7	-1660	-10.16
С	312	1028	190.0	18.3	80.8	0.9	-864	-10.17
М	267	879	A 45.1 B 48.2 C 71.6	16.4	82.6	1.0	-840	-10.28
Experimental (using 233 g of co				ns C):				
C	226	745	177.0		99.0*	1.0		

Table 8 Ge Fuming of 250 g Batch of Fargo Concentrate

TO BA

Ţ

2

+ "Fargo coal" is the coal fraction of the concentrate.

* Total Ge in gas, inferred from slag assay.

Table 9Results of Continuous Fuming at 1250°CUsing a Submerged Combustion Lance.

Inputs						_		0	utputs	_				
Rates/min. Totals		Slag			Fume*			Dust			Recoveryt			
Cons	Air	Cons	Air	Flux	wt.	% Ge	g Ge	wt.	%Ge	g Ge	wt.	% Ge	g Ge	÷
2.7 g	9.3 l	233 g	757 l	41.3 g	596	0.0005	0.003	1.5	3.65	0.055	2.4	0.61	0.015	99

• Only a fraction of the fume was collected.

SON

Ŀ

+ Recovery inferred from slag assay, showing 1% loss to slag.





ľ

÷.,

States and a second

