Quarterly Summary Report January- March 1978

Process for Cleaning and Removal of Sulfur Compounds from Low BTU Gases

April 1978

Pacific Northwest Laboratory
Richland, Washington 99352
Operated for the
U.S. Department of Energy
by

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.50
026-050	\$5.00
051-075	\$5.50
076-100	\$6.00
101-125	\$6.50
126-150	\$7.00
151-175	\$7.75
176-200	\$8.50
201-225	\$8.75
226-250	\$9.00
251-275	\$10.00
276-300	\$10.25

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PNL-2040-9
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OF SULFUR COMPOUNDS FROM LOW BTU GASES

by
R. H. Moore
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PROCESS FOR CLEANING AND REMOVAL OF SULFUR
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I. OBJECTIVE AND SCOPE OF WORK PHASE IV

In this phase of work the Process Development Unit (PDU) is to be remodeled by incorporation of appropriate subsystems to permit operation in continuous process mode. The PDU will be operated for a period of time sufficient to demonstrate process viability.

II. SUMMARY

1) Evidence has accumulated which indicated the $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 - \text{Li}_2\text{CO}_3$ ternary eutectic containing appreciable sulfide ion is much more corrosive than similar systems containing appreciable added CaCO_3 . It is concluded this is due to the tendency of Ca^{++} to combine with S^{--} to reduce the thermodynamic activity of the latter. The lowered S^{--} activity results in lessened corrosivity. CaCO_3 will be added at 20 mole percent to salt compositions employed in future PDU runs.

2) Activities were slowed by adverse weather during January and early February but it was possible to complete the following tasks in preparation for future operation:

Sampling and ΔP sensor lines to the extraction and regeneration columns were modified to reduce the frequency of plugging by solidified salt.

All (3) bellows sealed needle valves were removed and replaced by suitably modified gate valves.

Serious leaks at the base of the gasifier were repaired.

3) Run C-6 was initiated on 2/13/78. The extraction section was operated for only about an hour when flow through the venturi orifice became plugged

with corrosion products washed out of the extraction and regeneration columns and the coarse de-entrainer. The regeneration column was also operated for a short period on the reservoir of salt in the coarse de-entrainer.

4) Following Run C-6, the venturi was removed to permit installation of a CO₂ purge to the ¼ in. diameter x 1 in. long salt inlet orifice. The purge is introduced at about the middle of this 1 in. long orifice tube. The gate in the venturi flow control valve was also notched on the downstream side so the CO₂ purge on this valve will force salt out of the line and through the venturi orifice when the valve is closed.

5) Run C-7 was initiated 2/27/78 and gave indications that this modification of the venturi scrubber and feed valve would be successful in preventing further plugging of the venturi orifice. Unfortunately, this run was terminated prematurely following failure of the gas preheater.

6) Inspection of the gas preheater disclosed the electrical heaters had failed. When these were pulled for inspection, it was evident that this corrosive reducing gas environment had caused severe corrosion of the heater sheath alloy. Replacement elements have been ordered and should arrive here about 4/6/78.

7) During the enforced shut down for repair of the gas preheater, design of a salt filter and salt bleed recovery and recycle system was completed. The salt filter portion of the system has been fabricated and installed.

III. TECHNICAL PROGRESS

A. Consequences of Corrosion. Salt phase samples have now been analyzed in sufficient detail to permit the conclusion that severe corrosion of "aluminized" steel pipe and vessels has been occurring. The presence of corrosion products was detectable after but a few hours operation and it must be concluded that it is the corrosion products which have been responsible for most of the plugging problems experienced. This experience was totally unexpected and is in direct contrast to the experience obtained under the Office of Coal Research funded part of this program where the PDU was operated in batch configuration. At that time no evidence corrosion was observed and no corrosion products were ever detected in the molten salt.

Figure 1. Cross section of venturi feed line, 2X.

The differences then and now are minor but important: (1) There is a substantially larger area (a factor of 10) of metal exposed to the molten salt now than was true earlier, (2) CaCO_3 was present at about 20 mole percent in the salt employed in batch tests.

As the analytical data from runs C-2 through C-5 came in it became evident from the high iron content found in salt samples from various points that severe corrosion was occurring. The corrosion products formed a higher density, viscous, immiscible second phase which separated and collected at low points in the system. It appeared to be higher melting than the bulk salt and tended to solidify at cold spots to cause plugging.

Figure 1 shows the appearance of a cross-section of 1 in. pipe (actually of salt trapped in the seal ring of a grayloc hub assembly) filled with solidified salt. The black material was at the bottom of this nearly horizontal run of pipe upstream of the venturi feed valve. Assay of the black material disclosed 12.2 w/o Fe, 1.87 w/o Ni, 0.26 w/o Cr, and 0.49 w/o Al. The Fe and Ni were undoubtedly present as sulfides.

FeS can form relatively stable complexes with Na_2S which melt close to the operating temperature of 700°C . Examples of such compounds are illustrated by the phase diagram shown in Figure 2. Clearly, if these materials are being formed and are separating as an immiscible phase insoluble in the ternary carbonates, they could cause much trouble if they solidify in smaller lines, valve passages, and in the venturi inlet orifice.

CaCO_3 reacts with sulfide ion to form CaS. When present in the ternary alkali carbonates as solvent, reaction of added sulfide ion occurs almost exclusively with CaCO_3 until it is nearly completely consumed. Indeed, it is possible to show that CaCO_3 should inhibit corrosion of ferrous-alloys as a consequence of the following reaction:

Using thermodynamic data in the JANNAF tables¹ for CaS, CaO, CO_2 , and CO and data from Rosenquist² for FeS and for the incremental free energy of formation of CaCO_3 , equilibrium constants for the above reaction were calculated as tabulated in Table 1.

Figure 2.

Phase diagram of the system Na₂S - FeS.

TABLE 1. Equilibrium Constants for Reaction
of CaCO_3 with FeS

<u>Temp. °K</u>	<u>K</u>
800	0.0032
1000	0.09
1200	558

Due to the instability of FeCO_3 ,³ which decomposes irreversibly with oxidation by CO_2 to Fe_3O_4 , reaction (1) tends increasingly to proceed favorably as the temperature increases. This means that formation of FeS would be completely suppressed and corrosion of ferrous alloys would be inhibited.

Unfortunately, the serious corrosion of "aluminized" steels by the ternary alkali carbonate eutectic containing sulfide ion was not anticipated. Unquestionably, serious damage to PDU components has already occurred. In all future operations, CaCO_3 will be a major salt component and it is hoped that further damage can be avoided.

B. PDU Modifications. During runs C-2 through C-5, all of the ΔP sensors on the extraction and regeneration columns became plugged at one time or another. The associated sample lines also gave trouble with some becoming inoperative. Access to the columns for gas phase sampling and/or ΔP sensing is through a 3/8 in. schedule-80 pipe. A ceramic thermocouple protection sheath extends through this pipe into the columns and it was found that the annular space around this sheath was so small that even small amounts of salt could solidify in the annulus and cause plugging.

This arrangement was modified by replacing the ceramic sheaths with stainless steel of much smaller diameter. In addition the ΔP and sample take-off points were separated from the 3/8 in. schedule-80 pipe by a short length of 1 in. line to provide for salt condensation. All of this was heat traced so the salt can collect and flow back to the column.

In effect this modification extends the distance and enlarges the volume through which salt fume must pass before it reached a temperature at which solidification will occur. It is hoped this will suffice to solve the problem.

The bellows sealed needle valves for control of salt flow have all given serious trouble due to plugging. The $\frac{1}{4}$ in. diameter, Z-shaped flow path is easily plugged. What seems needed is a valve of the type which can be opened briefly to the full line diameter to dislodge a plug.

After much soul searching it was decided to procure stainless steel gate valves and modify them to allow their use in this severe environment. The valve stems and the housing around the stem were lengthened so as to remove the stem packing from the heated zone and provision was made for introduction of CO_2 purge gas around the stem so the salt would not rise to the level of the packing under its hydrostatic head.

The modified valves were welded into the spool pieces from which the needle valves had been removed to permit utilization of the grayloc hubs. When assembled into the lines, trace heaters and insulation were installed. These valves functioned very satisfactorily during runs C-6 and C-7.

C. Run C-6, 2/13/78. In preparation for run C-6, the salt was drained from the salt make-up pot and venturi feed tank. A fresh inventory of salt containing 20 mole percent CaCO_3 was then added (as solid salt) to the salt make-up pot and melted and brought to 700°C .

It is never possible to completely change out the salt. The extraction column holds a heel of about 6 liters if the siphon reservoir is empty and 9.5 liters if the siphon is full. The regeneration column holds about 5 liters and its siphon reservoir holds about 3 liters. The coarse de-entrainer retains a heel of about a liter.

Standpipes in the salt make-up pot and venturi feed tank cause retention of a permanent heel. This amounts to about 35 liters in the salt make-up pot and 7 - 8 liters in the venturi feed tank. The standpipe had been removed from the salt make-up pot following Run C-5 so this 35 liter heel was not present. In summary, the fresh salt inventory added at the start of run C-6, about 100 liters, would be contaminated by about 25 liters of salt originally present following Run C-5. This material was still seriously contaminated with corrosion products.

Run C-6 was initiated at 8:00 a.m. 2/13/78. Gas flow was valved to the PDU at 4:00 p.m. (2/13/78) but as pressure in the gasifier built up, the CO sensor suddenly alarmed and a leak was observed at the seal plate at

at the top of the lock hopper. Gas was by-passed while this plate was re-seated and then rerouted to the PDU with no further incident about 4:50 p.m.

Salt flow to the extraction column was started at 4:56 p.m. By 5:30 only 3 - 4 liters had flowed to the venturi feed tank. The gate valve was opened wider and in 7 minutes an additional 25 liters flowed to the venturi feed tank and the flow to the extraction column was hurriedly valved off.

Meanwhile, the venturi feed valve was opened but no evidence of flow was obtained. At about 7:15 a cold spot was detected in the venturi feed line. Additional insulation was added and at 8:45 p.m. flow suddenly started and rapidly drained the venturi feed tank (filling the salt cooler and the coarse de-entrainer).

Salt flow to the extraction column was resumed at 9:08 p.m. and by 9:14 p.m. 13 liters additional salt had been fed. Salt flow to the venturi resumed in a sporadic fashion but by 9:25 p.m. appeared to stop and despite continued efforts could not be restarted. It was necessary to valve off flow to the extraction column to prevent over filling the venturi feed tank. This was done about 10:00 p.m.

Salt flow was started to the regeneration column about 10:15 p.m. and this column was operated until the coarse de-entrainer emptied. Feed to the regeneration column could not be replenished with the venturi inoperative.

For the most part during this run the gas was passing through a static layer of molten salt on the trays of the extraction column. The venturi scrubber operated sporadically and for very brief intervals. Venturi operation was so uncertain it wasn't possible to get samples at times when it was operating.

Samples taken above the first (A-1) and second (A-2) trays in the extraction column and in the outlet line leading to the secondary burner (G-3) are compared with the average of inlet gas (G-1) analyses, Table I. Even though the PDU was not functioning properly, it achieved significant removal of sulfur compounds from a very dilute feed gas.

Salt samples taken from the salt make-up tank before and after run C-6 assayed <0.1 and 2.36 w/o Fe respectively. A composited sample taken from

TABLE II. H₂S and COS Analyses of Gas Samples from Run C-6

<u>Time Sampled</u>	<u>Sample No.</u>	<u>Sample Description</u>	<u>ppm H₂S</u>	<u>ppm COS</u>	<u>H₂S Rec. %</u>	<u>COS Rec. %</u>
3:05 - 4:07 p.m	G-1	Avg. Inlet Gas	409.5	188.5	-	-
6:03 p.m.	A-1	Above lower tray extr'n column	35	75	91.4	60.2
7:07 p.m.	A-1	Above lower tray extr'n column	97	13	76.3	93.1
10:25 p.m.	A-2	Above upper tray extr'n. column	16	76	96.1	59.7
7:21 p.m.	G-3	Final Product Gas	45	77	89.0	59.2
11:12 p.m.	G-3	Final Product Gas	51	77	87.5	59.2

the venturi feed tank midway through the run assayed 1.21 w/o Fe. At the time it could not be decided whether this iron was derived from the heel of severely contaminated salt from earlier runs or from continuing corrosion. The salt jettisoned following run C-5 had contained an average of 4.2 w/o Fe based on assay of salt in the salt make-up tank.

D. Modifications to the Venturi Scrubber. The only constriction left in the system is the 1/4 in. diameter by 1 in. long venturi inlet orifice. Earlier versions of the venturi scrubber had an orifice which was simply a hole through the wall of schedule-40 pipe, i.e. it was not very long. In this case, the venturi shape is determined by a ceramic insert which rests on a shoulder of steel about an inch thick and the orifice for entry of salt is drilled through this shoulder. The inlet angle is a steel shape and the throat and exit angle of the venturi are of ceramic.

Disassembly of the venturi disclosed the presence of black material plugging the orifice. To prevent repetitions of this problem a notch was machined in the wall of the venturi to provide a place to drill from and a hole was drilled to intersect the 1/4 in. x 1 in. orifice hole at its mid point and at right angles to it. A CO₂ purge line was welded in place.

Inspection of the Al₂O₃ liner showed it was holding up quite well though minor cracks were present. It was decided to replace it and after considerable difficulty in removing the old one this was done.

Finally, the gate in the venturi feed valve was removed and notched on the downstream side. This allows the purge gas on the valve stem to push salt out of the line between the valve and the venturi orifice when the valve is closed. By keeping this segment of the line clear of salt it would appear that plugging of the venturi orifice would be unlikely.

E. Run C-7, 2/27/78. Run C-7, also with 20 mole percent CaCO₃ present in the salt, was initiated at 2:00 a.m. 2/27/78. With this early start the gasifier was fueled and started about 11:00 a.m. and at 2:07 p.m. salt flow to the extraction column was initiated. Flow was maintained until the venturi feed tank filled at which point the valve to the extraction column was closed and the venturi feed valve opened. Immediate flow response was noted. The venturi feed valve was opened and closed several times during the next hour, and each time pressure readings indicated the CO₂ purge

flushed the line between the valve and the venturi orifice. This is the effect desired and it appears the plugging problem at the 1/4 in. diameter orifice may be controlled.

Intermittant addition of salt to the extraction column was continued until both the venturi feed tank and the coarse de-entrainer were full and full recycle flow was established in the extraction loop.

Efforts were underway to start flow to the regeneration column when about 4:00 p.m. it was noted that the data logger was printing an over temperature indication in the 2.5 in. venturi exhaust line just above the venturi. Investigation disclosed that the gas preheater was not heating and the trace heaters on the venturi exhaust line were picking up the task of heating the cold entering gas. Unfortunately, the molten salt catalyzes the Boudouard reaction, but at the low temperatures which prevailed, the position of the equilibrium favored carbon deposition (with loss of CO from the fuel gas). Soot buildup in the climbing film of salt in the venturi exhaust line formed a thick sludge which produced a condition resembling flooding wherein excessive salt is present in the venturi exhaust line. This resulted in excessive pressure drop across the venturi. A CO₂ purge of about 15 SCFM was blended in with the fuel gas, and for a brief period, this acted to suppress carbon deposition and the pressure drop returned to normal. As further cooling of the venturi exhaust line occurred (the trace heaters could not handle the heat load), soot deposition again became severe, the pressure drop increased and it became necessary to by-pass the gas flow and shut down the PDU.

It was not possible to establish flow to the regeneration column because a trace heater on the line coming out of the bottom of the coarse de-entrainer had failed and no salt would flow out of this tank. This trace heater could have been changed out without complete cool-down of the coarse de-entrainer but a delay of the run of several hours would have been necessary. In view of the difficulties with the gas preheater, it was decided to shut down all systems and effect repairs later.

Because of the short operating time, analytical data on this run was pretty skimpy. About midway through the run, a sample of the final product gas assayed 23.4 ppm H₂S and 17.5 ppm COS for an indicated recovery of 90%

and 86% respectively. Inlet gas assays were unusually low (229 ppm H_2S and 129 ppm COS) indicating the gasifier was not near steady state operation. Temperatures in the venturi section were lower than expected and not well known. Better than usual extraction of COS was obtained.

Salt samples taken from the venturi feed tank (16:50, 2/27/78) and from the coarse de-entrainer (17:40, 2/27/78) assayed 0.32 w/o Fe and 0.58 w/o Fe values significantly lower than found following run C-6. This is the first indication that the added CaCO_3 may be acting to inhibit corrosion. That the iron is lower is in part due to dilution by fresh salt added to make up losses due to inadvertant overflow at the venturi feed tank overflow standpipe. About 150 lbs of fresh salt was added. This amount of make-up salt is about average for each run and has resulted from problems with flow control through the venturi scrubber which we hope have now been resolved.

F. The Gas Preheater. Inspection of the gas preheater disclosed open circuits on all heating elements. When the heating element bundle was pulled, severe damage was evident. It appeared that the unit as a whole was nearing the end to its useful life due to generalized corrosion and carbonizing of the heating element sheaths. It was also evident that the unit had been overdriven and catastrophic failure of several heaters had occurred. The over-temperature protection thermocouple is clamped to one of the elements. If this element fails and cools, the over-temperature protection is lost. This may have been the reason for failure of the sort which involved so many heaters.

The internals involved are being procured from the original supplier and the heater should be back in service by 4/10/78. This is the planned date for start-up of run C-8.

G. Salt "Bleed" Recovery and Recycle. The sulfur extracting capacity of the salt can be regenerated by contact with steam - CO_2 in equipment specifically designed for this. Other impurities which accumulate in the salt, however, are not so easily removed. The most obvious means for control of such impurities is by means of a bleed stream and incremental additions of fresh salt.

With Li_2CO_3 @ 93¢/lb., K_2CO_3 @ 19¢/lb., Na_2CO_3 @ 3¢/lb., and CaCO_3 @ 1¢/lb. it will be desirable to recover and recycle Li_2CO_3 and K_2CO_3 . Na_2CO_3 and CaCO_3 cannot be economically recovered.

The chemical properties of these compounds and of the associated impurities requires the use of aqueous processing techniques for their purification and recovery. The design of a system for effecting the transition from a molten salt phase to an aqueous solution phase must take account of the serious problem of physical vapor explosions, or so called "superheat limit explosions" which occur when a molten salt is added to an aqueous phase. Because of the excellent heat transfer afforded by the intimate mixing of two liquids, vapor can be generated at a high rate. Under some conditions this may be accompanied by violent pressure pulses and shock waves which have proved to be fairly destructive in a number of instances.

Several theories have been proposed to explain the mechanism of vapor explosions. One of the most plausible involves a triggering mechanism initiated by collapse of the vapor film separating the hot and cold liquids. The collapse of the vapor film corresponds to the well known transition from film to nucleate boiling. If the hot liquid is dispersed in a cold liquid, the droplets of hot liquid will initially be coated with a film of vapor produced by vaporization of the cold liquid. As the hot liquid droplet cools the heat transfer rate becomes insufficient to maintain a continuous vapor film. When this occurs, the film will collapse allowing direct contact of the two liquids. Within a very short time following the collapse of the vapor film a sudden increase in vapor generation rate occurs and shock waves may be generated by the expanding vapor. This is accompanied by shattering of the droplets greatly increasing the surface and further increasing the vapor generation rate.

One theory holds that because of the lack of nucleation sites at the liquid - liquid interface, the cold liquid can be heated far above its normal boiling point. When the superheat limit or homogeneous nucleation temperature is reached, the liquid suddenly flashes. Because of the almost instantaneous conversion of liquid to vapor, shock waves may be generated. For a significant explosion to occur a relatively large mass of liquid must be present.

In Kraft furnace operation, the molten "smelt" at ~ 1500 F is quenched and dissolved in an aqueous liquor ("green liquor"). It is common practice to shatter the molten smelt with a steam jet or a spray of green liquor. This breaks the molten salt into small droplets which impinge on the surface of the liquor in the quench tank. Numerous small explosions result but the mass of material involved is maintained below dangerous levels. Various data are available which indicate that if the cold liquid is maintained at or near its boiling temperature, the probability of explosions is markedly reduced. In the design selected for the salt quencher-dissolver (below) the feature of hot liquid shattering and use of near boiling cold liquids is employed.

In the proposed design shown in Figure 3 salt, flowing through a heated nozzle impinges on a trough. The bulk salt stream flowing off the edge of the trough is blasted into droplets by liquid sprays of filtered salt solution. The salt/water slurry cascades over baffles which permit further cooling and dissolution of salt before the mixture falls into the boiling liquor reservoir below. Salt droplets washed off the baffle plates should be at or near their solidification temperature by the time they impact the boiling liquid reservoir. Experimental determination of salt phase and aqueous phase flow rates which lead to smooth operation will be possible. It will also be possible to change the number and configuration of baffle plates.

The proposed salt separation and recovery process takes advantage of the differences in solubility of the carbonates and bicarbonates. Sodium and potassium carbonates have relatively high solubilities and should be completely dissolved during the salt cooling and quenching step. CaCO_3 and Li_2CO_3 will remain associated with aqueous insoluble solids. The pH of this solution will be of the order of 9.5-10.0 which is sufficient to precipitate heavy metals as basic carbonates.

Figure 4 is a simplified schematic flow diagram of the proposed separation and recovery process. Table III shows stream flows identified by numbers in diamond shaped indices of Figure 4.

Stream 5 consists of precipitated solids which combine with suspended solids removed from stream 3. These are digested in a carbonator to dissolve lithium carbonate as LiHCO_3 which is several times as soluble as the normal carbonate. After solids removal, the LiHCO_3 solution is decarbonated by steam/air stripping to precipitate Li_2CO_3 which is removed by filtration.

Figure 3. Schematic of Quencher-Dissolver.

Figure 4. Schematic Flow Diagram. salt Bleed Recovery.

TABLE III. Stream Flows, lbs/lb of Salt Bleed, Cf. Figure 4.

Steam No.	Temp. °C	<u>H₂O</u>	<u>CaCO₃</u>	<u>Li₂CO₃</u>	<u>K₂CO₃</u>	<u>Na₂CO₃</u>	<u>KHCO₃</u>	<u>NaHCO₃</u>	<u>LiHCO₃</u>
1	700	-	0.20	0.26	0.26	0.26	-	-	-
2	35	1.47	Trace	-	-	-	0.48	0.04	0.01
3	100	1.47	Trace	0.01	0.74	0.30	-	-	
4	100	0.6	-	-	-	-	-	-	
5	35	-	0.20	0.26	0**	0**	-	-	
6	100	4.3***	Trace	0.03	2.2	0.9	-	-	-
7	20	10.4	Trace	-	-	-	-	-	0.57
8	20	10.4	Trace	0.31	-	-	-	-	-
9	20	-	0.20	-	-	-	0**	0**	0**
10	20	0.6	-	-	-	-	-	-	-

* Weight corrected to equivalent carbonate basis.

** Assumed 100 percent recovery.

*** Estimate based on 10/1 total collant/salt ratio.

The liquids from the primary centrifugation (stream 3) rich in Na_2CO_3 and K_2CO_3 can be carbonated to the bicarbonates which are much less soluble than the carbonates (contrast to $\text{Li}_2\text{CO}_3/\text{LiHCO}_3$). After removal of precipitated NaHCO_3 and KHCO_3 , the liquid phase is recycled to the quencher-dissolver. This liquid phase will also contain soluble silica as, e.g., sodium ortho-silicate. To prevent buildup of this material in the system, a portion of this recycle stream will have to be rejected as a waste stream. More detailed development of this recovery scheme has been deferred for the moment.

IV. PROPOSED WORK DURING THE NEXT QUARTER

It is planned to resume operation of the PDU using salt mixtures containing CaCO_3 for corrosion inhibition. Test runs will demonstrate the effectiveness of various demister (chemisorber) additions to the packed bed de-entrainer.

V. OVERALL PROJECT STATUS

Delays in completion of the PDU and work stoppages due to accessory equipment failures have severely delayed the program. Completion is now anticipated about mid June 1978.

VI. REFERENCES

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- (2) Rosenquist, T., "Thermochemical Data for Metallurgist" Tapir Forlag, 1970.

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