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DEVELOPMENT OF A SLURRY-FED IN-CAN MELTER FOR NUCLEAR DEFENSE WASTE

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ABSTRACT

In-Can Melting is the backup vitrification process for Savannah River Plant waste. A full-scale, non-radioactive process has been studied in which a slurry of waste sludge and glass formers is fed to a heated can. Saturated steam is used to cool the off-gas. Initial results show the concept to be viable.

SUMMARY

The Slurry-Fed In-Can Melter (SICM) was found to be a viable alternative to the joule-heated, continuous melter, the planned melter for immobilization of Savannah River Plant waste.

In the proposed SICM process, a 2-foot diameter stainless steel can is placed in a large tube furnace and heated to 1050°C. Waste sludge and glass frit are added as an aqueous slurry which dries and melts.

A glass melting rate of 74 lbs/hr was demonstrated (25 lbs/hr-ft^2). This is equivalent to an average processing rate of 40-54 lbs/hr, depending on the time required for the non-fill portions of the cycle. The SICM glass melting rate is high because the melt surface is exposed to the 1050°C walls of the can above the melt surface.

Injection of low temperature steam into the off-gas line was shown to be an excellent method of cooling the off-gas. Proper cooling of the off-gas was essential to prevent off-gas deposits which plugged the line with no off-gas temperature control. Steam cooling is the simplest system which will adequately cool the SICM off-gas. Steam cooling is also recommended for cooling the off-gas from other types of glass melters.

No more experiments are planned on the SICM at SRL. Future glass melter development at SRL will focus exclusively on the reference continuous joule-heated melter.

INTRODUCTION

The Savannah River Plant (SRP) has about 25 million gallons of high-level, radioactive, liquid waste stored in large waste tanks. This waste is a by-product of the production of nuclear defense materials at SRP. Plans are to build the Defense Waste Processing Facility (DWPF) at SRP to convert this waste to solid form.

A key step in the planned DWPF process is the vitrification or glassmaking step, in which the radionuclides are converted to borosilicate glass. Two types of glass melters have been developed for this step. The planned melter design for the DWPF is a slurry-fed, continuous, joule-heated melter. The backup melter design is an in-can melter.

Previous plans were to dry the radioactive waste sludge before feeding it to the in-can melter. However, it was desirable to eliminate the drying step and feed the waste sludge as a liquid. Eliminating the drying step simplified the process and reduced the project cost.

To test the liquid-fed process, a full-scale, non-radioactive in-can melter of the former dry-fed design was converted for slurry feeding. Five experimental runs were made with this process from August to December 1981. The purpose of the program was to develop and demonstrate a full-scale SICM process for the DWPF.

This paper describes the conclusions of this initial process study of the SICM.

PROPOSED DWPF SICM PROCESS

A 2-foot diameter, 304-L stainless steel can - the standard DWPF can - is placed in a large tube furnace (Figure 1). The combination off-gas/feed line is connected to the can, and a slight vacuum is established on the can. The annulus between the can exterior and the furnace is purged with argon. The argon protects the can exterior from oxidation. The furnace is heated to 1050°C. The temperature is limited to 1050°C because above this temperature 304-L stainless steel is not strong enough to safely withstand the process.

Waste sludge and glass frit are added to the can as an aqueous slurry. The slurry falls to the surface, dries, and then melts. Saturated steam is injected near the opening of the off-gas line to cool the off-gas exiting the can from 900°C to 450°C. After the can is filled, the furnace is maintained at 1050°C for six hours. This allows the glass to homogenize. Then the furnace is cooled and the can is removed.

The SICM process differs from other slurry-fed, in-can melter processes in that the entire can is heated. In slurry-fed, in-can melter processes developed for power reactor waste (for example, the HARVEST process developed in Great Britain) the can wall above the melt line is kept cool to limit the off-gas temperature and melt surface temperature. In the DWPF SICM process, the entire can is heated, and the off-gas is cooled by steam injection. This results in a higher melt rate.

SICM Rate

A key objective of the SICM experimental program was to develop a relatively high rate process. A high rate for the DWPF melter is important because of the large volume of waste at SRP, about 25 million gallons, which must be processed.

The maximum glass melt rate demonstrated in the SICM program was 74 lbs/hr with a 40% solids slurry. This corresponds to a melt flux of 25 lbs/hr-ft^2. This rate is high because the melt surface is exposed to the 1050°C can walls above the melt line. Calculations show that 60-70% of the heat to the melt comes by radiation from the can walls above the melt line.

The SICM average rate depends on the time required to complete each part of the SICM cycle. The total cycle time for a reference can was estimated to be between 60 and 81 hours. This is equivalent to an average rate of 40 to 54 lbs/hr. About 4 to 6 SICM melters would be required to meet the DWPF glass production rate, assuming equal reliability of the DWPF process with the SICM melter or the continuous melter.

The spread in the estimated cycle times was caused by the uncertainty in the permissible temperature limit for canister removal. This limit affects both the estimated heat up and cool down times. Therefore, selection of the permissible temperature limit for removing a can has a major impact on the SICM cycle time and average rate.

Cycle Time Estimates

The SICM cycle consists of five distinct periods - 1) fill period, 2) bake-out period (the time from the end of the fill period until the furnace is shut-off), 3) cool down period, 4) can change period, and 5) heat-up period. Each of these periods was studied in a non-radioactive experimental furnace at SRL. The time required to complete each period was estimated as follows:

- The fill period required 44 hours, corresponding to a rate of 74 lbs/hr in filling a 3260-pound can. In the experiment that this rate was demonstrated, the rate was maintained despite the failure of two-thirds of the heaters in the top three feet of the furnace. This indicates that 44 hours is a conservative estimate of the time required for the fill period.
- The bake-out period required 6 hours. About 2 hours at temperature were required for the entire contents of the can to heat up to 1050°C. The remaining 4 hours were required to ensure that the glass near the can top homogenized.
- The cool down period required 4 to 20 hours. The time required for the cool down depends on what temperature is permissible to remove the can from the furnace. If a 700°C canister wall temperature limit is used, 4 hours of cooling are required. However, current guidelines for design of the DWPF call for a maximum glass centerline temperature of 600°C before lifting. This is a much more conservative limit, requiring a 20-hour cool down period.
- The can change period was estimated to require 2 hours. This period was not studied in the experimental melter. However, the accuracy of this estimate is not important because the can change period is short compared to the rest of the SICM cycle.
- The heat-up period required 4 to 9 hours. The variation of the period is also a function of the permissible temperature limit

for can removal because the heatup starts at the same temperature that the can is removed.

Off-Gas Deposits

The SICM program demonstrated that cooling of the off-gas and insulation of the off-gas line are necessary to prevent accumulation of deposits inside the SICM off-gas line.

The off-gas from the SICM is mostly water vapor and non-condensible gases - primarily oxygen, carbon monoxide, and carbon dioxide, plus air and argon that leak into the off-gas line. However, the off-gas also contains small quantities of particulates (frit and waste sludge particles) and semi-volatile materials evaporated from the molten glass.

Previous experience with continuous melters had shown that the particulates and semi-volatiles tended to deposit in the off-gas line, causing plugging problems. Therefore, this was anticipated to be a potential problem in the SICM experiments. The frit becomes sticky and tends to deposit when the off-gas temperature is above the frit softening temperature - about 475°C. The semi-volatiles tend to deposit more as the temperature decreases. Therefore, maintaining the off-gas slightly below the frit softening temperature is desirable.

The first experiment with the SICM (SICM-1) demonstrated the need for off-gas cooling. No cooling was used in this run. An attempt was made to limit the off-gas temperature by keeping the top of the can cool. However, due to the construction of the furnace, this was not possible. The off-gas temperature 3 feet downstream of the can was 600-850°C, much higher than the target of 450°C.

Deposits, projecting up to 3/4-inch from the pipe walls, formed in the off-gas line (Figure 2). Several clumps formed after the first bend. A second deposit formed after the first 90° bend. Both of the deposits formed only on the less than vertical surfaces of the pipe. They appeared to have formed from sticky frit particles in the off-gas which settled from the off-gas and stuck to the pipe. These deposits appeared to have formed in the disturbed flow regions following the bends. By far the worst deposit formed about 35 feet downstream of the melter at a spot which had inadvertantly been left uninsulated. This deposit filled the entire 6-inch off-gas line indicating that a cold spot greatly accelerates deposits. This deposit was probably caused by a combination of sticking frit and semi-volatile condensation.

Very little accumulation was found other than at these three spots. A very thin glassy film less than 0.01 inch was found in the first two feet of the off-gas line. Elsewhere in the line, a light non-glassy dust was found, mostly on the bottom of the pipe. The light deposits also tended to form only where particles in the off-gas would fall by gravity to the off-gas pipe surface.

Steam Cooling of the Off-Gas

Steam injection cooling is the simplest system that will adequately cool the SICM off-gas. Steam cooling successfully eliminated off-gas line deposits in the SICM. The main disadvantage of steam cooling is that it increases the water load to the melter off-gas system. Other methods of cooling the off-gas that will introduce less water into the off-gas are available. But these methods are more difficult to implement than steam cooling.

A steam injection cooling system was used in all except the first SICM experimental runs. Steam was injected about 2 feet downstream of the can into the off-gas line (Figure 2). Injecting steam at the entrance to the off-gas line would have been preferred, but piping the steam to that point would have required considerable modifications to the melter.

Figure 3 is a schematic of the system that supplied steam to the off-gas line. Steam was supplied by a 150-psig steam header. The steam flow was regulated by an automatic valve controlled from the SICM control room. The temperature of the off-gas downstream of the steam injection point was measured using a thermocouple, which sent a signal back to the control room. A condensate valve just ahead of the flow regulating valve prevented liquid water from entering the melter. The operator running the SICM monitored the temperature downstream of the steam injection point and adjusted the steam flow to maintain that temperature as described.

This system was found to be an excellent method to control the off-gas temperature and was successful in eliminating deposits (Table 1). In the SICM, the off-gas temperature at the can top was about 900°C. The steam injection system could cool this to any desired temperature and was used to maintain the off-gas temperature 3 feet downstream of the can at about 440°C. The off-gas temperature remained steady at a constant feed rate and could be easily maintained by manually adjusting the steam flowrate every 10-15 minutes. With this system in use, no more off-gas line deposits formed downstream of the steam injection point.

The main disadvantage of steam cooling is the high steam rate required. The SICM requires 1.7 to 2.2 pounds of steam per pound of uncooled SICM off-gas. This is 330-440 pounds/hr of additional water per melter which must be evaporated later in the process. The required steam rate is large because of the high SICM off-gas temperature. The present DWPF flowsheet cannot accommodate this increased water load, and additional evaporation capacity would need to be provided in the flowsheet to handle this SICM process.

Further development work might reduce this water load, possibly through the use of a water spray system or air injection. PNL has experimented with water spray systems for cooling continuous melter off-gases. These require much less water than steam, but the method of injection is critical. Deposits form quickly if water impinges on the wall of the off-gas line. The design of such a water spray system is more critical, and it would probably require more maintenance than a steam injection system. Air injection would also decrease the water load relative to steam, but causes other off-gas flowsheet complications.

Steam injection cooling has also been recommended for cooling the off-gases from other waste glass melters, especially continuous melters. Because the off-gas temperature at the melter exit is much lower in a continuous melter than in a SICM, the amount of cooling steam needed is much less. Steam cooling is therefore more attractive for a continuous melter than for a SICM. Steam cooling is the simplest and least troublesome method to cool the off-gas, when the flowsheet will accommodate the increased water load.

Off-Gas Line Connection to Can

Perhaps the greatest challenge in the SICM is the connection of the can to the off-gas line. This connection must be made and broken once each cycle, and the design of the connection is critical. The connection is prone to off-gas pluggage because it is the transition between the hot can and the much cooler off-gas line. The connection must resist corrosion by the off-gas or be protected from the off-gas. Also, the connection must be compatible with further processing of the can.

The connection between the can and the off-gas line used in runs SICM-1 through SICM-4 worked well (Figure 4). This connection, which is the off-gas line extending through a hole in the canister top plate, was used because it was simple and inexpensive. Initial SICM runs were intended to look at other parts of the SICM system. Less than 0.01 inch of black glassy deposits formed in the bottom three feet of the off-gas line during these runs. The very small amount of deposits was surprising because the line was not cooled in this region and was probably 800°C to 1000°C; therefore, considerable deposits were expected from sticking of softened frit. A possible explanation for the small amount of deposits is that material deposited, but the temperature was high enough to melt the deposit and cause it to drop back into the can.

In the last SICM experimental run, deposits plugged the off-gas line near the can. This run was the first and only attempt to use a reference DWPF can in the SICM. The bottom 24 inches of the off-gas line which formerly entered a 6-inch diameter hole was redesigned to fit the smaller 5-inch diameter reference nozzle. This left an annulus of only 1/2-inch through which the off-gas could pass because the feed tube assembly was located in the center of the off-gas line. Although this was not considered an optimum arrangement, it was judged adequate because of the lack of deposits in previous runs. The off-gas annulus filled with glassy deposits about 2 inches above the can top. The deposits must be related to the different can top and redesigned off-gas line, but no good explanation exists for the greatly increased deposits.

More work is needed to better understand what happens at the connection of the can and off-gas line and develop a connection that will fit a can with a reference nozzle. The best option at this time appears to be injection of the off-gas cooling medium into the bottom of the off-gas line right at the can connection. Thus, the off-gas line would have no uncooled section, eliminating the frit sticking problem. Several methods to accomplish this are being considered for the DWPF continuous melter, the reference melter. Any of these methods would be candidates for the SICM.

SICM Feed Composition

The feed composition used in the high rate run is shown in Table 2. This simulated waste composition is representative of the average anticipated SRP waste composition, which is called "Stage 1 simulated waste" at Du Pont. The glass frit was the frit 140 composition. This frit was developed at SRL specifically for in-can melting. The composition is very similar to frit 131, a frit developed for continuous melting of SRP waste. The simulated waste and frit were mixed in the ratio 35/65. The waste and frit were at 41% total solids in water.

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TABLE 1

SICM OFF-GAS COOLING SYSTEM RESULTS**

	SICM-1	SICM-2	SICM-3	SICM-4
Steam injection used	No	Yes	Yes	Yes
Deposits downstream of injection point	Yes	No	No	No
Average flow rate (lbs/hr):				
• Uncooled off-gas	160-190	DNA	180	180-200
• Steam injection	0	DNA	300-375	330-440
Lbs steam per lb of uncooled off-gas*	0	DNA	1.7-2.1	1.7-2.2
Off-gas temperatures during feeding (°C)				
• 3 feet downstream	600-850	400-460	400-460	440±10
• 20 feet downstream	580-750	320±20	375±45	390±10
• 100 feet downstream	300-530	250±20	305±45	360±10

DNA - Data not available

* Steam was saturated at 150 psig

** Data not shown for SICM-5 because deposits in off-gas line entrance prevented stable operation of off-gas system.

TABLE 2

SICM-4 FEED COMPOSITIONS

FRIT 140

COMPONENT	WT %
SiO_2	60
B_2O_3	16
Na_2O	14
Li_2O	5
MgO	2
Al_2O_3	0.6
CaO	1.1
Other	1.0

STAGE 1 SLUDGE

COMPONENT	WT %
$Fe(OH)_3$	51
MnO_2	11
$CaCO_3$	8
$Ni(OH)_2$	3
$Al(OH)_3$	21
Coal	0.1
Zeolite	6.2

Sludge/Frit ratio: 35/65

Total Solids in Slurry: 41%

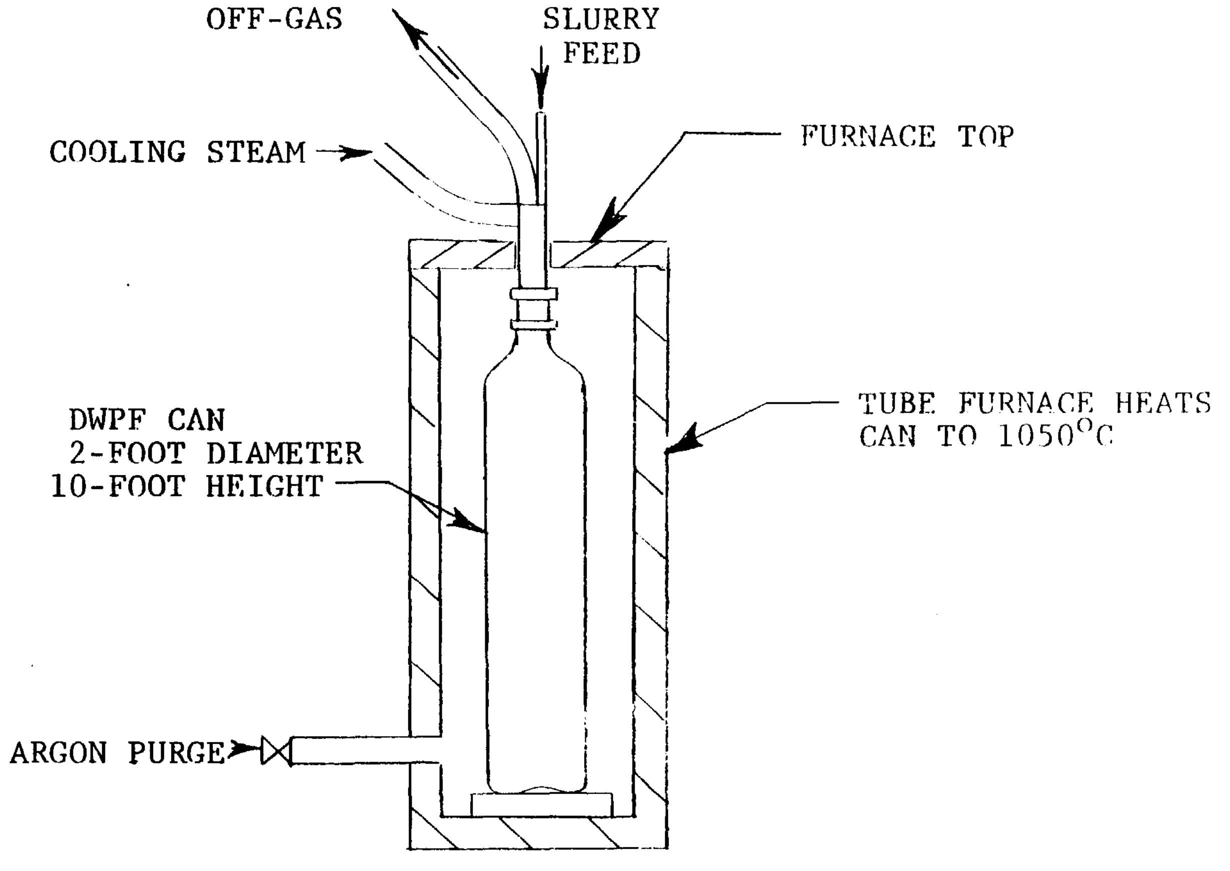

FIGURE 1. SICM Conceptual Process

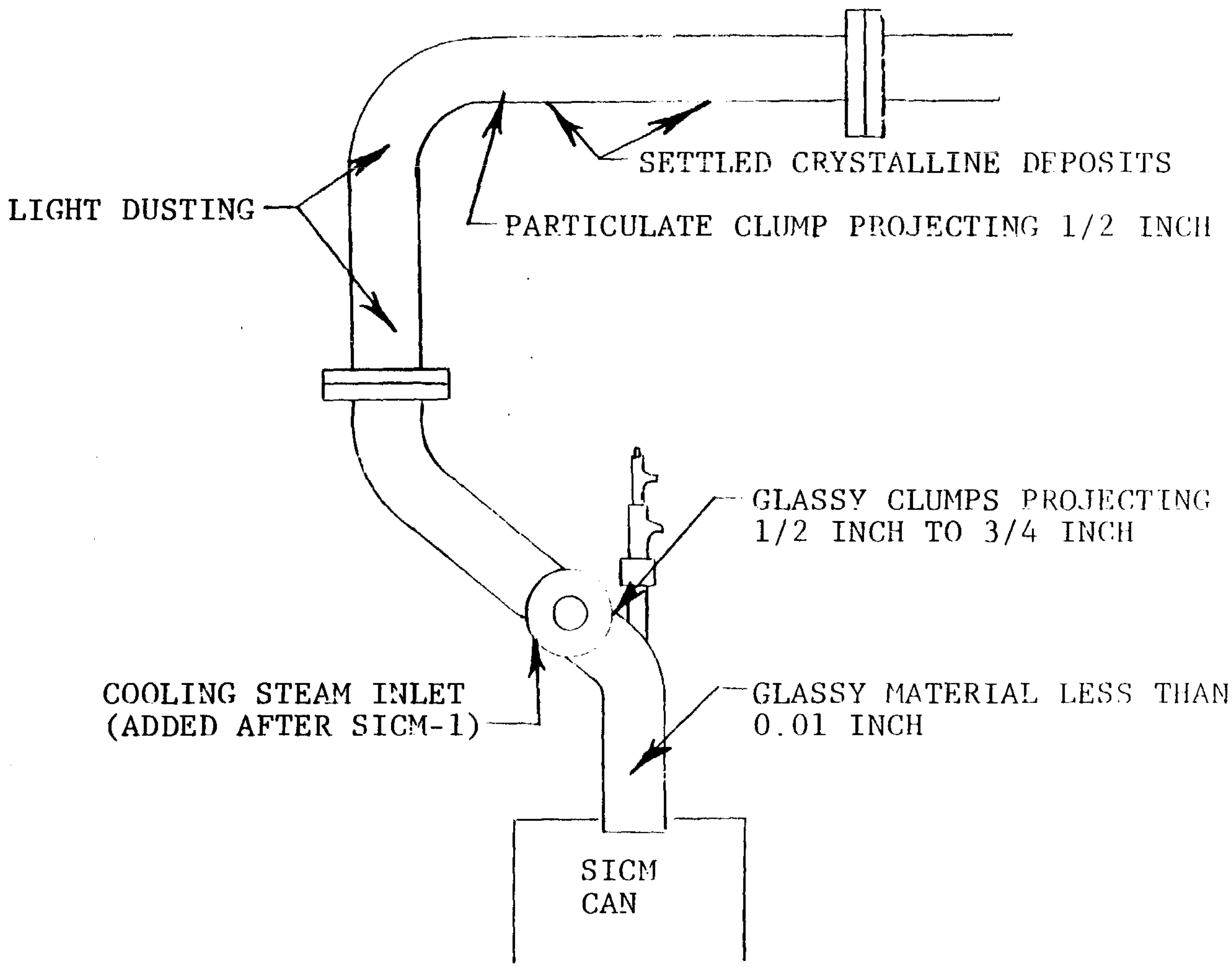

FIGURE 2. Off-Gas Deposits After SICM-1

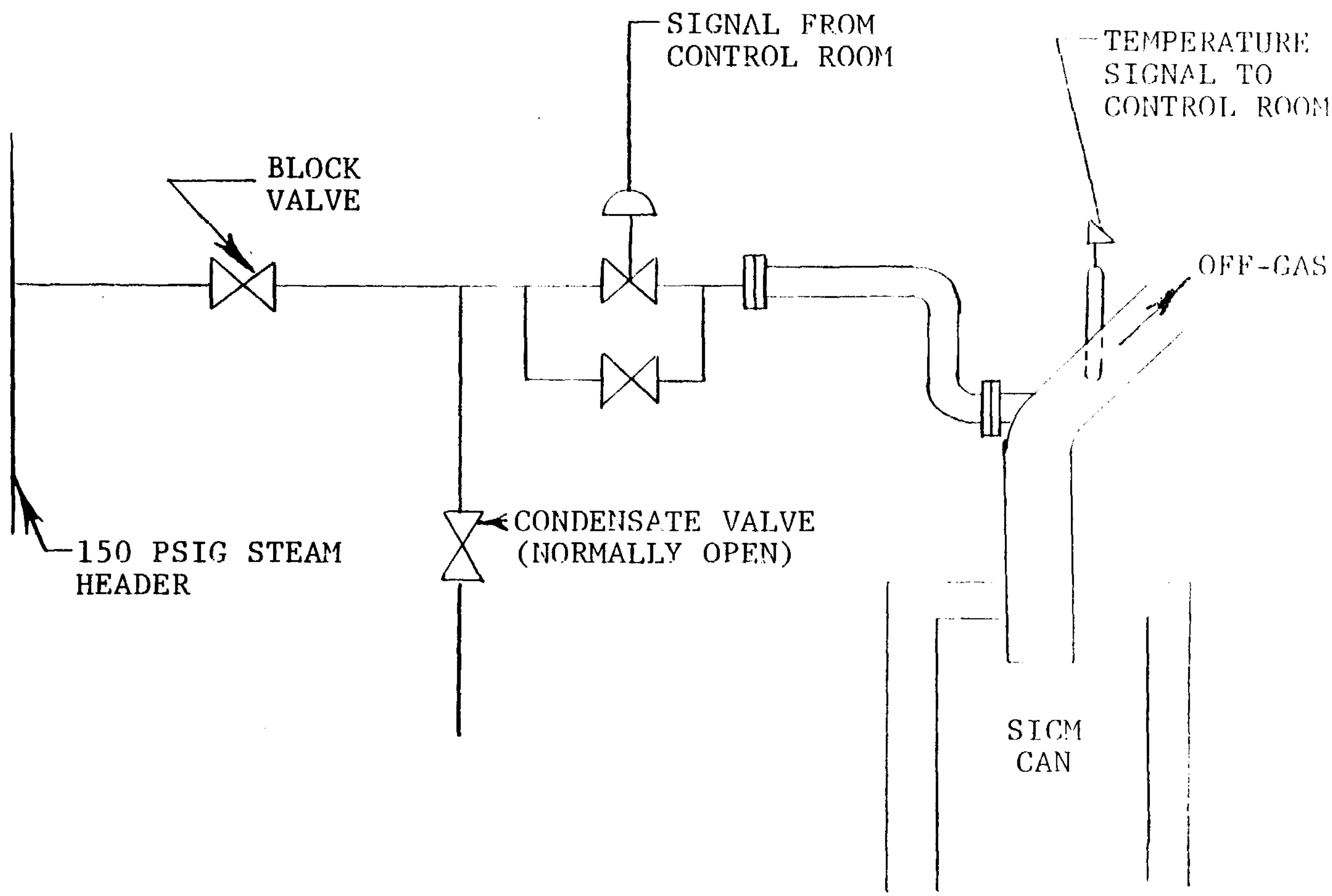

FIGURE 3. SICM Off-Gas Cooling System

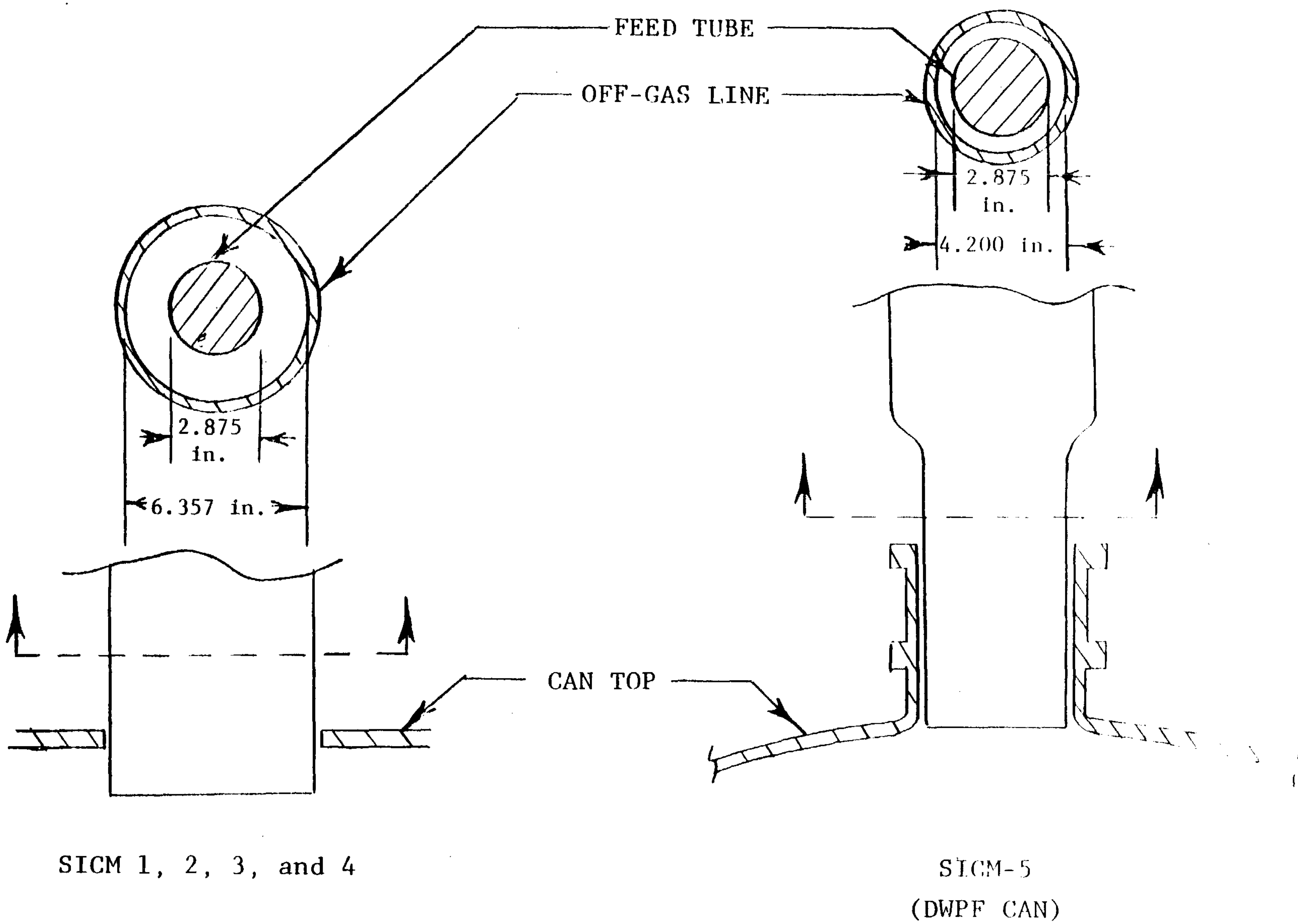

FIGURE 4. SICM-5 Modifications