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DEVELOPMENT OF VITRIFICATION TECHNIQUE OF HLLW IN ENGINEERING SCALE AT PNC

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ABSTRACT

Some processes have been investigated to develop the technology of solidification of the high level radio active liquid waste generated from the nuclear fuel reprocessing plant at PNC. This report covers the present state of development of a joule heated ceramic melter and a direct megahertz induction heated furnace.

An engineering scale test has been performed by both of these melters. A joule heated melter could treat 45 kg glass an hour or 16 l/hr. A direct induction furnace was able to melt 5 kg glass per an hour or 1.8 l/hr. Both of the melters were composed of refractory ceramics and electro-fused cast. Therefore, glass could be melted at above 1200°C. At the higher temperature melting, the glass would be the more reliable, in general.

1. Introduction

The high level liquid waste generated from PNC's reprocessing plant is assumed to have rather high concentration of sodium nitrate about 1 mole/ℓ from the solvent regeneration cycle. If the aimed glass contains 30 wt % waste equivalent to waste oxides, the concentration of sodium oxide might be 10% in glass product. About 10% of sodium oxide in Borosilicate glass is considered to be a limit on its quality assurance, especially on water resistance leach rate.

The glass compositions used were as follows:

First and third campaigns;

SiO_2 43, B_2O_3 14, Al_2O_3 4, Li_2O 3, CaO 2, ZnO 2 and waste 30%

Second campaign;

SiO_2 54-50, B_2O_3 9-12, Al_2O_3 5, Li_2O 2 and waste 30% in weight

The waste composition above is detailed as follows;

Rb_2O 0.204, Cs_2O 1.3684, SrO 0.5474, BaO 0.907, Y_2O_3 0.337, La_2O_3 0.784, Ce_2O_3 1.529, Nd_2O_3 3.833, Other Rare Earth Oxide mixture 2.608, ZrO_2 2.6754, MoO_3 2.66, TeO_2 0.343, MnO_2 0.39, Fe_2O_3 1.792, Cr_2O_3 0.172, NiO 0.513, CoO 0.157, Na_2O 9.18, Total 30% in weight.

In an early stage of the solidification programme, HLLW might be calcined and feed into glass raw material. For this purpose, the calcination process such as fluidized-bed and spray is being developed in other programme. In fluidized-bed clacination process, alumina would be added to stabilize the calcination behaviour. And also fluidized-bed material may be mixed with these calcined waste, such as silica, alumina. The amount of components of mixed calcined process silica and alumina as well as soda is to be considered as necessary raw materials.

To produce a homogeneous glass, it is preferable to select comparatively higher temperature melting process, such as ceramic melter.

An engineering scale direct joule heated ceramic melter was demonstrated. And also a mega-hertz direct induction heated ceramic melter was operated. Through these operations, the designation principles were realized and performance of refractories and electrodes was evaluated.

2. Joule Heated Ceramic Melter

As the joule heated ceramic melter heats in glass melt, the hottest part exists in the midst of the electrodes in molten glass and the covered batch layer prevents to heat dissipation. And also this batch layer may contribute to trap of the volatile matters from feed itself and glass melt. At the same time, as the refractory block may be kept at lower temperature than a glass melt, a corrosion of side wall by glass melt can be reduced.

The waste contained glass shows very strong darkening. Therefore, melting by the conventional radiation heat is difficult. Because the infrared ray is absorbed only on the glass surface and does not reach into deep layers. This fact limits the glass melting depth to only several centimeters deep, then it is impossible to carry out a large scale glass melting. [1]

Metallic molybdenum endures a strong thermal shock and high electric current density. The problem of using Molybdenum is its easy oxidation and sublimation at higher than 800°C as MoO_3.

We had adopted the molybdenum and tin oxide electrode in this experiment. Figure 1 shows the design of the direct joule heated ceramic melter which has the following specifications:

(1) Molybdenum electrodes at a melting zone were set. Two pairs of electrode 50 mm in diameter were equipped with 75 kW electric power supplied.

(2) At a rising zone behind the throat, a pair of molybdenum 32 mm in diameter was adopted, of which role was to control the temperature of pulling out glass.

Both electrodes of molybdenum were covered with a water-cooled jacket.

(3) Tin oxide electrodes,63 mm in diameter, were set at forehearth where they might be exposed to air above the glass level.

(4) Total holding capacity of glass is 200 liter. The minimum glass holding is 100 liter to maintain the joule heating.

2.1 Heating up and steady run

The furnace was heated up to 1200°C for 3 days by SiC heater of 38 kW in a melter and $MoSi_2$ of 15 kW supplied in a forehearth, both of which were suspended from super structure. Heating up rate was 15°C/hr. After it reached to 1200°C, glass cullet and raw material were charged into the melter. Molybdenum electrodes were set off behind the side wall and kept water-cooled before the glass level rose above the electrode and then inserted into the final position. (Fig. 2.)

The electric resistance R assumed from outside between electrodes was calculated according to Gailhbaud [2]. The relation of R and specific resistivity of molten glass ρ was

$$R/\rho = 0.0552\ \mathrm{cm}^{-1}$$

by the geometrical arrangement of the melter in Fig. 2.

Raw materials batch calcined were supplied by an automatic vibrational feeder which moved cyclically back and forth and charged the raw powder over the entire surface. Feed rate of dry raw batch was 45.3 kg glass equivalent per an hour in average and 54 kg/hr at maximum when electrical power supplied in the melter was 35 - 50 kW.

Heating up and steady run conditions are tabulated in Table 1, where holding level means to hold as low level and keep idly without feeding raw materials.

2.2 Slurry supply

Simulated high level liquid waste mixed with glass frit was supplied as slurry slip directly into the melter by pumping up of a mechanical tubular pump. Slurry supply experiments made at third campaign for a week. Volume rate supplied was 30 - 60 ℓ/hr where 3 liter of wastes with glass additives converted to 1 kg glass. After the slurry was poured into the melter, the surface was covered with liquid completely where the bubbling was continued violently from the sintered layer. When the glass level descended, the sintered layer would often form bridges or vacant domes between batch and molten glass. Increasing the glass level, the slurry was supplied at a rate of 60 ℓ/hr without any bridge formed. Stable feeding rate was determined 50 ℓ/hr in 0.3 m^2 melting surface or 167 ℓ/m^2·hr.

2.3 Performance observed

On the first campaign, the future operated at 1200°C for 3 weeks and produced about 2.5 ton of the glass to cast into 13 canisters. The corrosion depth of refractories was rather small. However, after the second campaign of melting temperature at 1350°C for 4 weeks to melt 4.8 ton of the glass, these refractories have been corroded in 12 mm deep maximum in the case of melter blocks of AZS electro-fused cast Zirconia silica alumina, but the corrosion of chrome zirconia brick (S 216) have not been determined. The maximum corrosion depth occurred 5 to 10 cm above electrode level, where the maximum temperature region existed.

Upward drilling was found at the throat 10 to 12 mm in depth. As a result, AZS fused cast block might be corroded at a rate of 0.25 mm/day at initial stage. There appeared several cracking on the surface of refractories.

These cracks were concentrated near the glass surface line where severe thermal shock was often happened due to temporary supply of the wet slurry.

Reduction and oxidation reaction between molybdenum and molten glass were observed. Thermodynamically, molybdenum is oxidized in the waste contained glass at high temperature and nickel, tellurium, cobalt oxides etc. are reduced to metal. Therefore, metallic precipitation must be synthesized in glass melt touched with molybdenum. In fact, this precipitation was appeared on the bottom of the melter and on the surface of molybdenum electrodes. The consumption of the electrodes would be almost negligible, as far as these campaigns.

Compared with the long life basin part of the melter, the superstructure equipped with some electric sensor, heater and glass flow controlling mechanism would not be so long lived, and therefore, periodical maintenance and parts substitution must be needed under hot running (hot repair). So the built-in super structure must be prepared as a whole substitutional repair. Further development of the furnace has been undertaken.

2.4 Concepts of hot operation

Heating up the furnace under cold or inactive condition and setting it in a steady state of continuous melting, then all operations will be completely remote-controlled and the furnace will be run under hot condition. Once the furnace is operated hot, the ceramic bricks would be severely contaminated with hot particles by diffusing from glass, therefore, the joule heated ceramic melter must have a long life and must be continuously operated for a long term more than a year. The expected furnace life would be two years.

As melting capacity is large enough to treat the generated HLLW from a several tons equivalent per day reprocessing plant, the melter may be kept idly as low glass level and also as low level in activity, but holding glass must be kept as melt at enough temperature.

3. Mega-hertz Induction Furnace

High frequency induction melting comprise "direct" and "indirect" heating of glass, the former represent the heating of glass itself by high frequency induction and the latter is the induction heating of metal pot. Direct induction melting enables the use of ceramic pot as a melting container, which provides the high temperature and long term melting.

Authors have performed the test operation of the direct induction melting for two years with a middle scale pilot plant.

3.1 Middle scale pilot plant and its operation

Figure 3 illustrates the middle scale pilot plant assembly. Raw material consisted of the simulated waste and glass frit was supplied to the ceramic pot by a constant feeder located under the hopper. In the ceramic pot, a starting rod made of SiC was suspended at the center. At the initial stage of melting operation, the starting rod was heated by high frequency of 4 MHz, supplied through a work-coil installed around the pot. A 4 MHz, 65 kW high frequency generator was provided to supply the high frequency power to the coil. After some amount of raw material was melted and the high frequency came to oscillate the glass melt, the starting rod was pulled up above the glass line. Direct induction melting realized at this stage. Melting of the raw material can proceed when it supplied continuously through the constant feeder. After the melt reached to 80% level of the pot, then the nozzle installed at the bottom of the pot was heated by indirect induction heating of SiC ring with high frequency of 300 KHz. For this indirect heating, 15 kW high frequency generator was also provided. The melt come out from the nozzle was stored in a metal canister located under the nozzle of the pot. Dust filters and a duct are connected to the off-gas pipe installed in a furnace cover. Another pipe was also installed at the furnace cover for the measurement of the melt temperature by a radiation pyrometer.

Control panel was prepared, in which output powers and work coil current were controlled and recorded.

Table 2 shows the operational data of the direct induction melting. The start-up was easily performed for 6 kg of the raw material by indirect heating of the SiC rod with about 30 kW anode output. The time for the start-up depends on the thermal shock resistance of the pot material. When a silica pot is used, the start up can be accomplished within one hour.

The capacity of the direct induction melting with a 35 to 40 kW anode output was about 6 kg/hr when the pot size was 200 mm in inside diameter. The capacity depends upon the pot size and temperature of the melt. Above value was obtained when the melt temperature was kept at 1200°C. The melting capacity increases to 7.5 kg/hr for the pot with inside diameter of 230 mm.

Direct melting can proceed by continuous supply of the raw material at above capacity. Thus, the melting capacity of this pilot plant is estimated to be 50 - 60 ℓ/day according to the pot size. Test operation of the pilot plant proved above capacity, except the actual capacity reduced 40 - 50 ℓ/day because of the time consumed for the pull-out operation of the melt.

3.2 Performance of the furnace

One of the important factors to consider in the melting process is life of a refractory, in this case, the ceramic pot. Various pots made of sintered silica, fire clay, or fused cast Zirconium-aluminate were used in long (10 days) continuous test operation. The sintered silica pot was corroded considerably, and the pot life is assumed to be around 10 days. Pot made of fire clay or fused cast refractories showed no sign of corrosion, thus, considering the corrosion of those refractories experienced in the glass industry, the life of those pots is estimated more than 6 months.

3.3 Possibility toward full-scale active plant

Direct induction melting was performed successfully at the middle scale plant. This advantageous process has merits in the simple furnace structure and ease of operation and remote control. Many problems, however, still remain in order to scale up this process to a full-scale active plant.

Remote control and remote maintenance of the plant are the major subjects for the future work. At the same time, considerations should be placed on the connection of the melting process to the equipment of raw material supply and off-gas system.

4. Conclusion

The joule heated ceramic melter was operated in three campaigns totally for 58 days and melted 8 ton glass with 30% equivalent simulated at 45 kg/hr in average. Slurry supplied experiment also have been performed. Performance of the melter was evaluated over more than a year including idling time.

The direct mega-hertz induction furnace was equipped and successfully melted glass at a rate of 5 - 7.5 kg/hr and the life of ceramic touched with melt would be longer than a half year.

The glass products obtained from both processes were shown to have good homogeneity and to be high quality.

References

[1] E.V. Tooley (Ed.), Hand Book of Glass Manufacture, Vol. 2 Ogden Publ. Co., N.Y. (1960)

[2] J. Gailhbaud: Glastechn. Ber., 45, 56-67, (1972)

Table 1 Stable Operation Conditions of Ceramic Melter

	Rising level				Holding level			
	Power kW	Volt	Amp.	Temp. °C	Power kW	Volt	Amp.	Temp. °C
Melter	46.8	85	550	1150	40.9	95	430	1140
Riser	6.0	63	95	980	3.2	45	70	1020
Forehearth	0.5	21	23	1100				
Orifice	2.1	41	50	800	0.4	13	28	
Forehearth super	8.4	43	195	1030	9.9	44	225	980
Bowl super	6.5	33	197	850	4.2	24	172	940

Table 2 Operation Data of Direct Induction Melting

Pit size		
Inside diameter, mm	200	230
Outside diameter, mm	230	260
Height, mm	550	550
Start-up with SiC rod		
Frequency, MHz	2.8	2.5
Anode Output, kW	20	22
Anode current, A	3.7	3.5
Anode voltage, kV	5.3	6.0
Work coil current, A	160	180
Raw material to start, kg	10	14
Time for start-up, min.	60	70
Melt temperature, °C	1150	1150
Direct induction melting		
Frequency, MHz	2.8	2.5
Anode output, kW	39	42
Anode current, A	5.6	6.0
Anode voltage, kV	7.0	7.5
Work coil current, A	120	120
Melt temperature, °C	1200	1200
Melting efficiency, kg/hr	5.5	7.5
Melt pull-out		
Frequency, kHz	300	300
Anode output, kW	6.3	6.3
Anode current, A	0.9	0.9
Anode voltage, kV	7.0	7.0

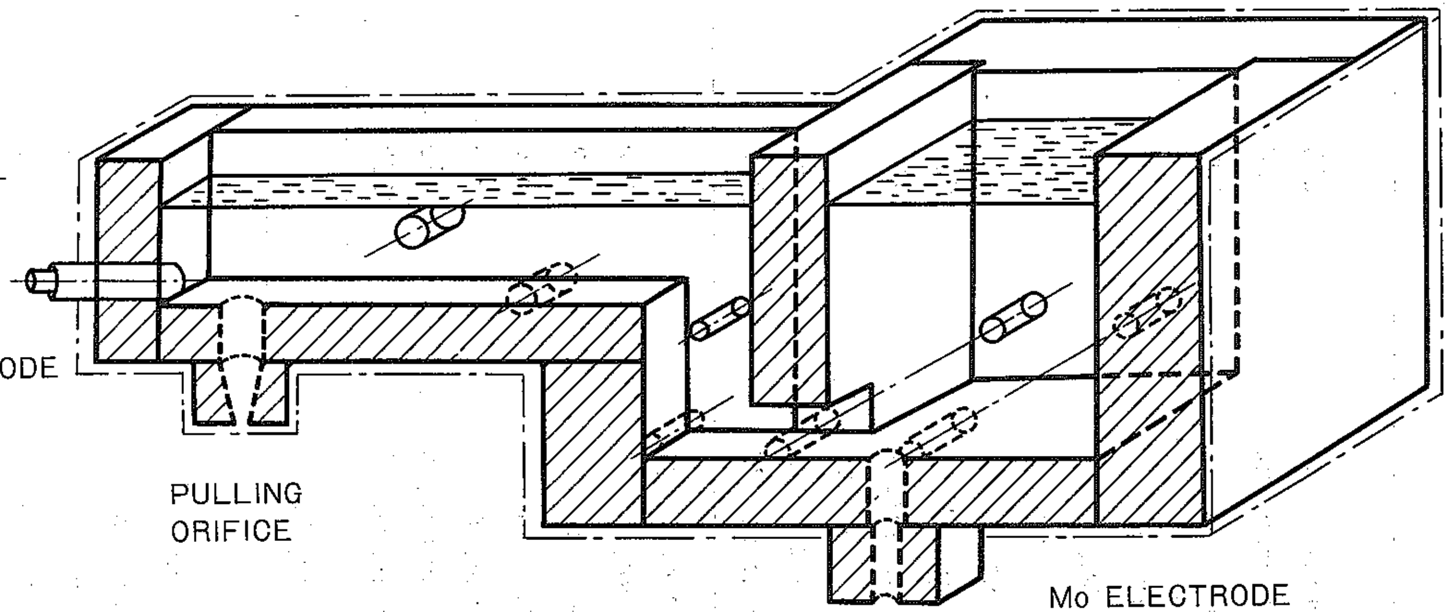

Fig. 1 Schematic of Joule Heated Ceramic Melter.

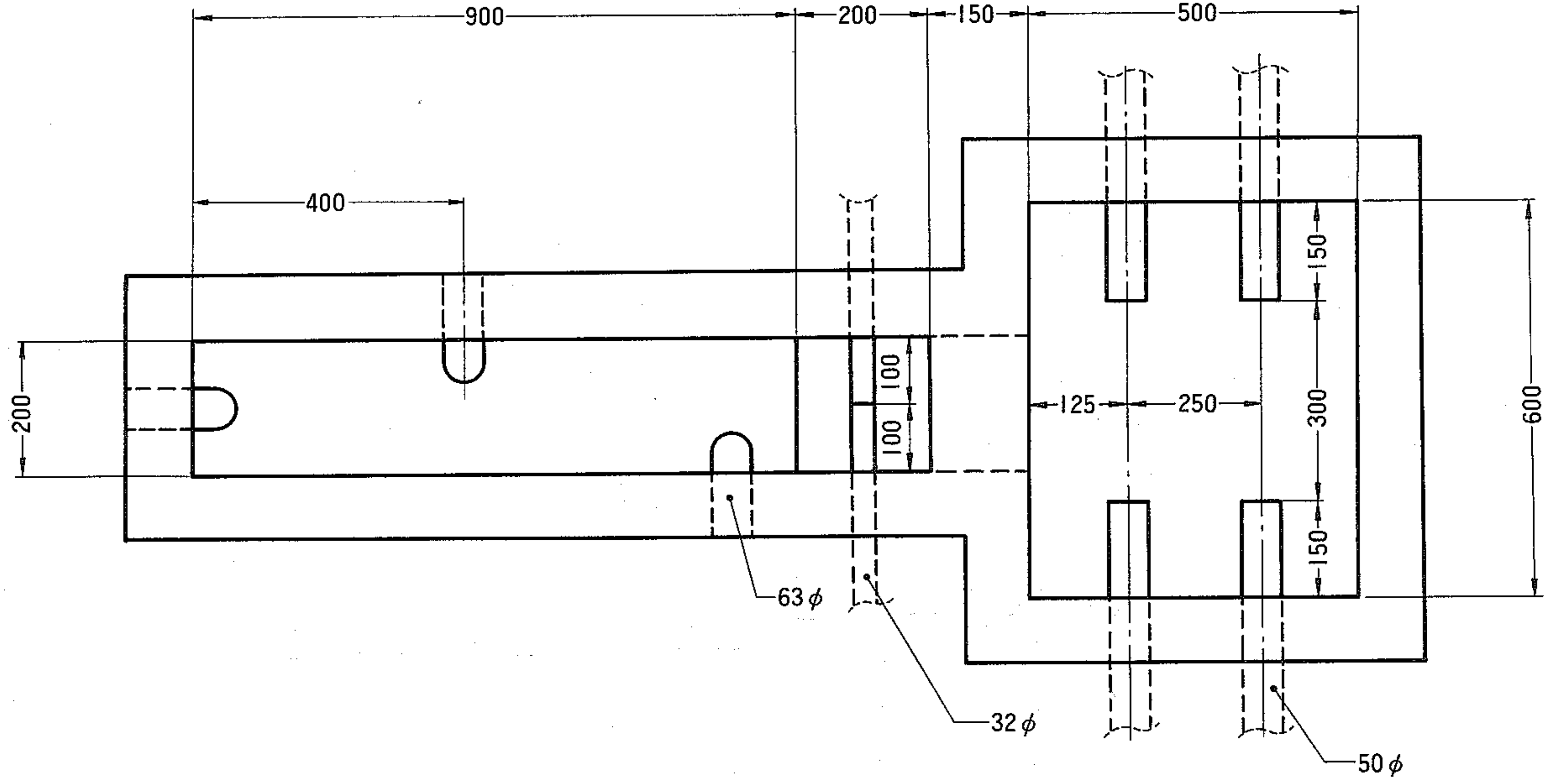

Fig. 2 Plane Figure of Engineering Scale Ceramic Melter.

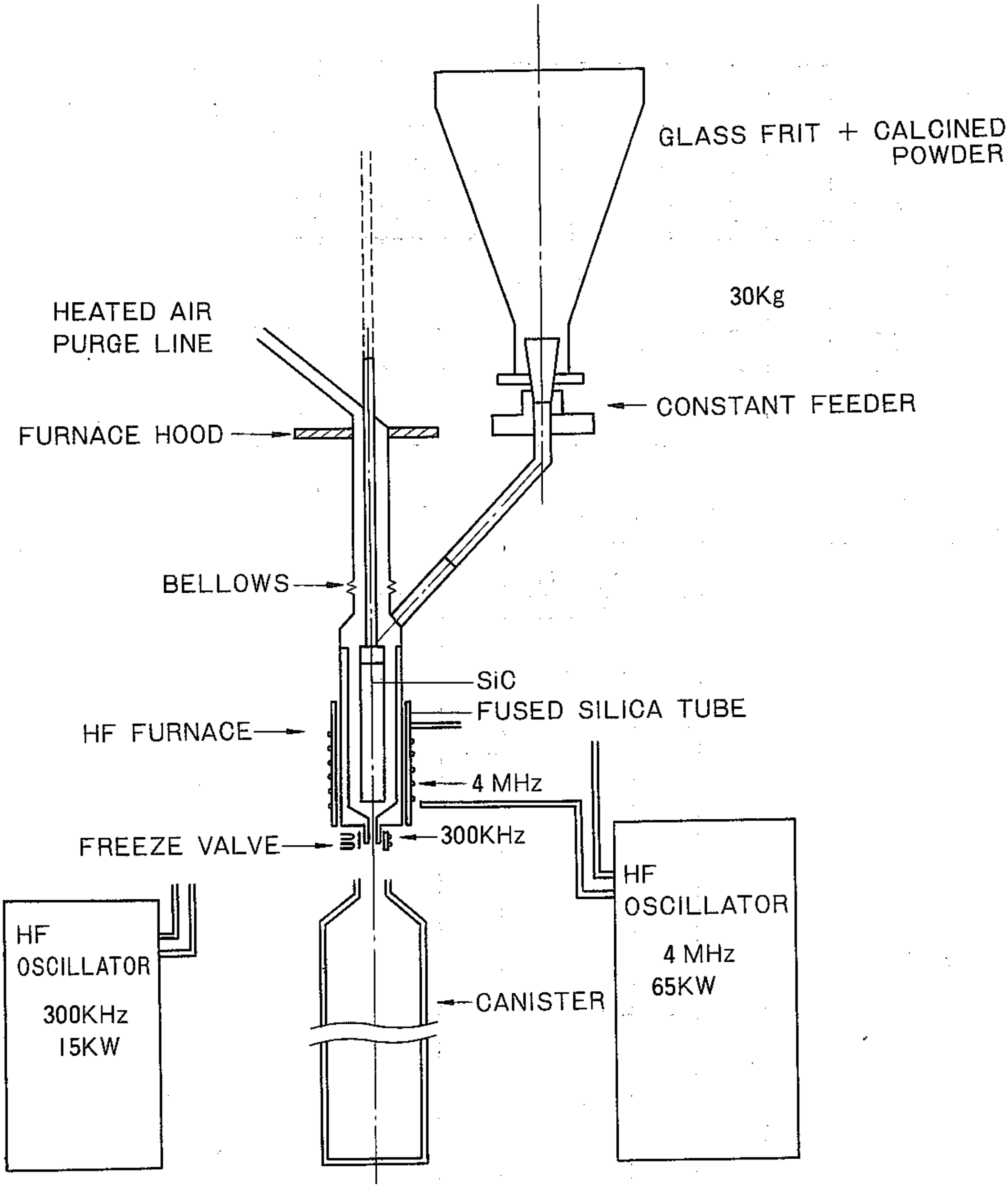

Fig. 3 Middle Scale Direct Induction Melter.