Proceedings of the Korean Nuclear Society Spring Meeting
Pohang, Korea May 1999

Vitrification of Surrogate Non-radioactive Waste Using a Bench-Scale Cold Crucible Melter

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Abstract

KEPCO(Korea Electric Power Corporation) is responsible for safe operation of nuclear power plants. One of its social responsibility is, thus, the safe storage and ultimately, complete isolation of radioactive waste from the environment. However, selection of disposal site is very difficult in Korea as well as in other countries with vast amount of land. In this regard, NETEC/KEPCO launched a research project for developing a high volume reduction technology, i.e., vitrification process. The objective of this paper is to present test results which were obtained in a small scale cold crucible melter(CCM) in order to acquire basic design parameters for design of the pilot plant of 1/4 scale of the commercial vitrification plant. The tests were performed in Marcoule, France using the induction melter of diameter of 300 mm combined with an off-gas treatment system. Ion exchange resin, combustible dry waste, and boron concentrates were simulated and vitrified. The experiments showed that the direct vitrification process could effectively destroy organic compounds in the waste and the off-gas could be treated in compliance with the environmental regulation. Maximum capacity of the CCM was found to be 12 kg/h. Off-gas characteristics such as flow rate, temperature and dust concentration had been measured, based on which the pilot vitrification plant of the maximum throughput of 50 kg/h was designed. It is under construction to be completed by the first half of the year and pilot tests will be carried out with a view to develop vitrification process for commercial plant.

1. Introduction

Solid radioactive waste is generated during operation and maintenance of nuclear power plants. It should be safely treated and disposed for protection of human and environment. However, it has been only processed and stored on site since a disposal site is not available. Thus, KEPCO was forced to develop a new treatment technology which can significantly reduce waste volume, compared with the conventional methods commercially available.

A feasibility of the application of vitrification process to low-level radioactive waste for nuclear power plants was studied. Protective clothes, surgeon gloves, etc were vitrified with borosilicate glass in the laboratory-scale melter and their mechanical characteristics of the vitrified waste were analyzed. Volume reduction was found to be around 60 or higher for cotton which is the major composition [1] of dry active waste generated from nuclear power plants. It was concluded that low-level radioactive waste volume could be reduced to around 1/20 of the volume as collected if plasma torch system is combined with the cold crucible melter to treat both combustible and non-combustible waste including filters.

Based on this feasibility study, a research project for the development of a commercial vitrification plant was launched in 1996. As a first step toward this goal, the cold crucible melter of diameter of 300 mm(Fig. 1) and the off-gas treatment system were established to fully evaluate the feasibility of the vitrification process and finally obtain parameters necessary for the design of the pilot plant. The objective of this paper is to examine main experimental results from the small-scale vitrification facility in Marcoule, France.

2. Experimental Setup

A schematic of the bench-scale vitrification apparatus is shown in Fig. 2. The main component of the system is the induction melter of diameter of 300 mm. It was made of stainless steel and its wall is cooled during operation. Thus, thin film of solid glass is formed on the inner surface of the melter, which prevents from chemical attack from corrosive material contained in the waste.

Electric energy is delivered inside the melter by a high frequency generator of 240 kW and converted to thermal energy to melt glass and destruct organic compounds of the wastes which are fed on top of the glass melt. Inorganic elements in the waste are incorporated in the glass which is poured to a container for analysis. Volatile material and gases resulting from the reaction in the melter are drawn to a post combustion chamber(PCC). It is an electrically heated chamber designed for a two second residence time at 1,100℃ to complete the combustion reaction and thermally destruct hazardous chemicals in the off-gas such as dioxin.

The off-gas from the PCC is drawn to the offgas treatment system by an extraction fan which keeps the whole system at a slightly negative pressure in order to prevent untreated gas from leaking out to the work place. The offgas process system consists of a quencher, an air dilutor and a scrubber. High temperature gas from the PCC is passed through the quencher where the gas is rapidly cooled down to 80℃ after air dilution. Any particulate entrained in the off-gas is filtered out in Venturi scrubber. Acid gas such as SO_x is absorbed in the scrubber. The processed offgas is then released to environment.

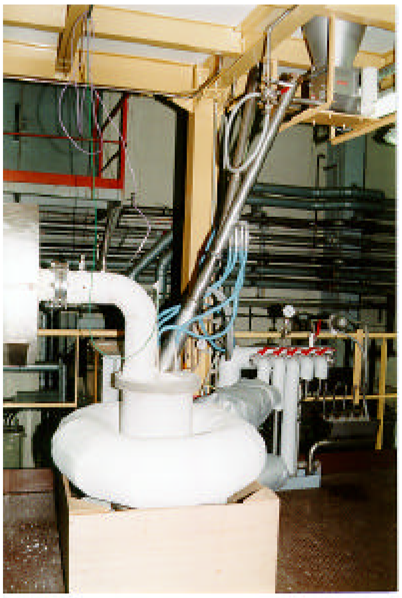


Fig 1. Photo of the Bench-Scale CCM

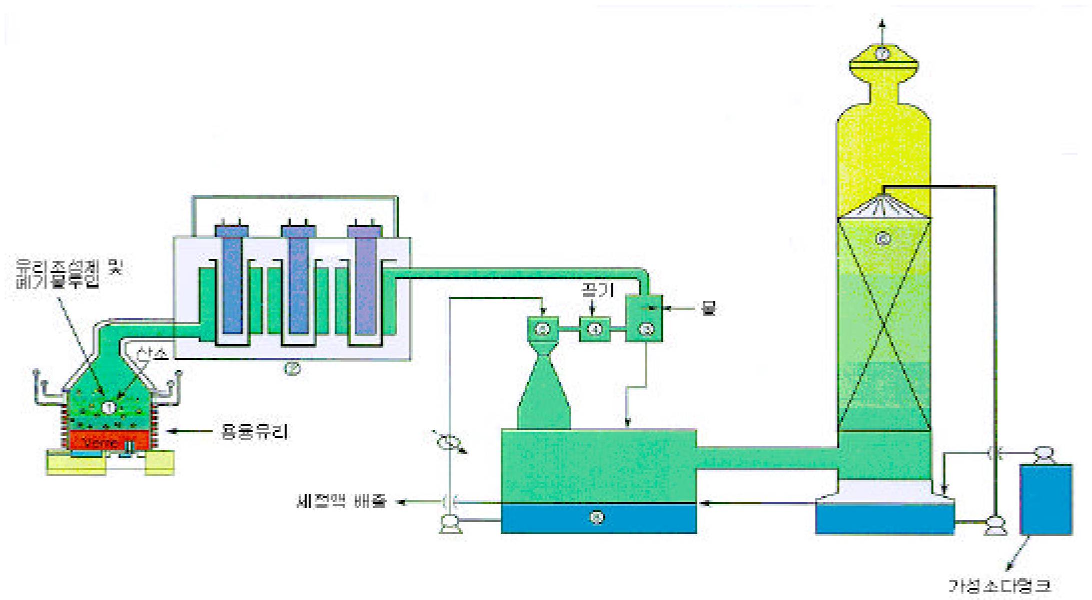


Fig 2. Schematic of the Offgas Treatment System

2. Preparation of Waste

Ion exchange resin, combustibles and simulate borates were used for the tests. However, vitrification of ion exchange resin is described in this paper. Its elemental composition is described in Tab. 1. Additives such as Co, Cs, B, Li were loaded to fresh material in order to simulate actual waste.

Table 1. Elemental Composition of Resin (W/O)

Type of Resin	C	H	O	N	S
Duolite ARA	74.9	9.2	6.0	5.4	-
IRN 78	61.3	9.5	15.7	5.3	<0.3
Duolite ARC	58.5	4.87	22.0	-	14.6
IRN 77	45.5	4.3	32.7	<0.1	13.6

There are many kinds of glass historically used for vitrification of high-level radioactive waste. Borosilicate has widely been recognized [2] for its good characteristics in terms of process operation and the stability of the waste form. Therefore, borosilicate(Tab 2) was chosen at first and then Nepheline which has no iron and boron contents was used for testing possible reduction of the dust entrained in the offgas.

Table 2. Chemical Contents of the Glass (W/O)

Type of Glass	SiO_2	Na_2O	B_2O_3	Al_2O_3	Fe_2O_3
Borosilicate	46.5	20.0	18.5	10.0	5.0
Nepheline	54.0	28.0	-	18.0	-

4. Process Operation and Measurement

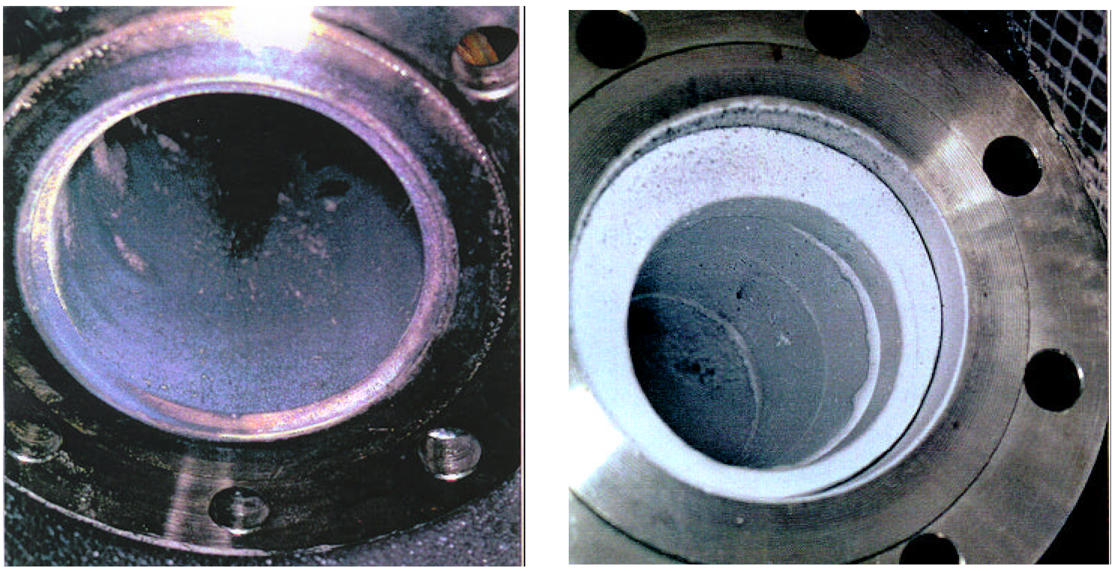
At first, glass frit is fed into the CCM and then, a small Ti ring is introduced on top of the glass. The ring is heated by the electric current induced by the high frequency generator and thermal energy is dissipated from the ring to the glass. Its electric characteristics are started to change. Temperature increase of the glass is then rapidly accelerated by induction of electric energy to the glass directly by the generator. Excessive oxygen(25~50%)or air is also injected to the upper chamber of the CCM to help combustion of the waste. Mixing of the glass is boosted by air or oxygen bubbling to the glass melt from the bottom of the CCM. During the feeding of the waste, glass temperature is maintained at about 1,250 ℃.

Status of combustion in the CCM was periodically checked through the attached sight glass and monitored by measuring CO and CxHy contents in the offgas at the exit of the CCM. Dust contents, gas concentration, temperature and flowrate were measured to investigate offgas characteristics and evaluate performance of each offgas equipment. Glass samples were taken from the bottom of the CCM for chemical analysis with X-ray diffractor, ICP, AA, etc. Physicochemical properties of the vitrified waste associated with waste form stability are in the scope of the future research work. CO_2 concentration in the offgas was analyzed with infrared analyzer after removing condensed water and particulates with 2 μm filter. CO and NO were measured with the electrochemical sensors. An isokinetic sampler was used together with 47 mm glass fiber filter whose collection efficiency was 99 % or higher for particulates of 0.2 μm or greater. Size of particuletes entrained in the offgas was measured with an eight-stage cascade impactor separately collecting dust of between 0.35 μm and 7.5 μm.

5. Test Results

Destruction of Organics

Pure oxygen proved to be much more efficient in combustion of organic material in the waste than air. This was clearly shown by the fact(Fig. 3) that inside of the CCM and its outlet pipe was much more clean with pure oxygen injection compared one with air feeding in which case unburned black deposit was observed on the inner surface of the associated pipe.



With Air Feeding　　　　With Pure Oxygen Feeding

Fig. 3 Dust Deposit on the Inlet Pipe of the PCC

Determination of the Maximum Capacity

Maximum capacity of a CCM may be determined by various factors such as diameter of CCM, electric capacity of the high frequency generator, the offgas characteristics, etc. Dust contents and CO concentration at the CCM outlet steeply increased at feed rate of around 10 ~12 kg/h for resin and combustibles. Thus, it was concluded that its maximum process capacity would be 12 kg/h.

Characterization of the Offgas Characteristics

Since combustion of resin and combustibles is exothermic reaction, gas temperature at CCM outlet increased almost linearly with feedrate. Fig. 4 shows offgas temperature versus waste feedrate. In case of resin vitrification, offgas flow rate from the CCM was measured to be about 27 Nm^3/h including air inleakage of 5 Nm^3/h. During steady state operation, CO and CxHy concentration at the CCM outlet was less than around 200 ppm, 50 ppm respectively. This could be a direct indication of good combustion of organic contents in the waste. In startup period, however, concentration of CO exceeded 600 ppm which is the release limit to the environment due to the low temperature in the CCM. SO_2 and NO were found to be 6000 ppm, 2000 ppm respectively. The former was not detected at the outlet of the scrubber whereas the latter was not effectively removed in the scrubber. Hence, selective catalytic reduction bed was proposed to be installed in the pilot plant to reduce NOx contents in the offgas.

Dust contents were in the range of 1~10 g/Nm^3. It seemed that many factors could affect amounts of dust entrained in the offgas. They depended on the velocity of oxygen injected, glass type, etc. Particulate was less entrained in the offgas with Nepheline than with borosilicate glass. Boron contained in borosilicate seemed to volalitize easily at relatively low temperature. During pilot tests further study will be carried out for optimum selection of the glass type. Measurement of the size distribution revealed that 85 to 90 % of dust was less than 3.1 ㎛. The dust was identified to be mostly $CsLi_5(SO_4)_3$ by X-ray diffraction analysis. Entrainment factor for Co, Cs needs to be precisely evaluated in the pilot test.

High temperature filter made of Al_2O_3 was added to the offgas treatment system for effective dust removal. Its removal efficiency was measured to be 99.9 %. Keeping the temperature of the filter above 150 ℃ was identified to be one of the critical factors to the efficiency. Below this temperature, the efficiency was reduced due to condensation of the offgas on the filter media.

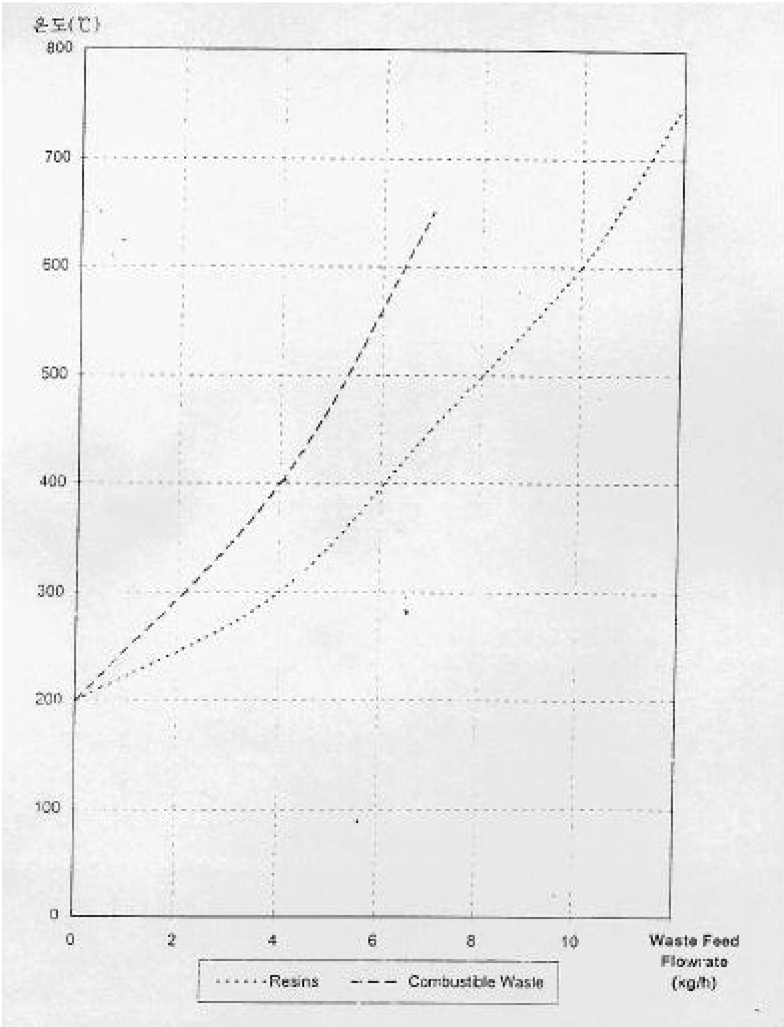


Fig. 4 Offgas Temperature against Feedrate of Waste

Properties of the Vitrified Waste

Phase separation was found in the glass when no air was injected into the glass melt. Air or oxygen injection through the bottom of CCM greatly improved glass homogeneity. Oxygen-injected glass was analyzed and compared with the air injected glass(Tab. 3). The former was found to be more effective in oxidation of metal components and expulsion of C and S which were known to be limiting factors [3] to the glass quality.

Table. 3. Glass with Oxygen and Air injection

items	glass with oxygen injection	glass with air injection	remarks
SO_3	0.5 %(surface) 0.3 %(bottom)	0.98 %(surface) 0.44 %(bottom)	
FeO	2.65 %(surface) 2.45 %(bottom)	3.8 %(surface) 2.55 %(bottom)	
C	<0.01 %(surface)	0.45 %(surface)	
Redox	0.78 %(surface)	0.93 %(surface)	(Fe^{+2}/Fe^{+3})

6. Conclusion

Surrogate inactive ion exchange resin was successfully vitrified in the CCM of 300 mm diameter and the offgas could be treated in compliance with environmental regulation except NOx. Through the bench scale tests, basic design parameters such as maximum capacity of the CCM and offgas characteristics were obtained for design of the pilot scale vitrification plant. Based on these tests, the pilot plant was designed. It is under construction(Fig 5) and is planned to be completed by the first half of 1999. Thereafter, pilot tests will be carried out until the beginning of 2000. During this period, process optimization study will be performed including determination of optimum oxygen feedrate, entrainment factors for major radionuclides and performance of the offgas treatment equipment will be tested.

Fig. 5 Pilot Plant under Construction

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