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## IMPROVEMENT OF MELTER OFF-GAS DESIGN FOR COMMERCIAL HALW VITRIFICATION FACILITY

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The Japan's commercial reprocessing plant is now under construction, and it will commence the operation in 2005. The High Active Liquid Waste (HALW) generated at the plant is treated into glass product at the vitrification facility using the Liquid Fed Joule-Heated Ceramic Melter (LFCM). The characteristic of the LFCM is that the HALW is fed directly onto the molten glass surface with the glass forming material. This process was developed by the Japan Nuclear Cycle Development Institute (JNC).

The JNC's process was first applied to the Tokai Vitrification Facility (TVF), which is a pilot scale plant having about 1/6 capacity of the commercial facility. The TVF has been in operation since 1995. During the operation, the rapid increase of the differential pressure between the melter plenum and the dust scrubber was observed. This phenomenon is harmful to the long-term continuous operation of TVF. And, it is also anticipated that the same phenomenon will occur in commercial vitrification facility.

In order to solve this problem, the countermeasures were studied and developed. Through the study on the deposit growing mechanism, it was probable that the rapid increased differential pressure was attributed to the condensation of metaboric acid at the outlet of the air-film cooler slits. And, the heating and the humidification of purge air were judged to be effective as the countermeasures to suppress the condensation. On the other hand, the water injection into melter off-gas pipe was found to be very effective to reduce the differential pressure as the results of the various tests. The deposit adhered on the inner surface of the off-gas pipe was almost washed out. And, it was also demonstrated that the system was superior to other systems by virtue of its simplicity and stability.

In order to apply the system to the commercial scale plant, the scale-up tests were conducted at JNC's mock-up facility using the acrylic model. As the result of the scale-up tests, the water cleaning system was also verified to be effective for the commercial scale melter. And, the optimum pipe configuration and the operating conditions were also evaluated. In conclusion, it was determined that these improvements were applied to the commercial vitrification facility, and the results of the scale-up tests were incorporated in the design.

## INTRODUCTION

In the process of HALW solidification, several steps are included such as evaporation, denitration, calcination, and dissolution into molten glass. Generally, calcination is performed in the temperature range from 300°C to 800°C and preparation of glass at 1000°C to 1200°C. In the LFCM process, the waste and the glass forming material are fed on the top of molten glass where all the necessary steps take place. In these processes, the off-gas generates from the top of the molten glass. The off-gas contains mainly air, water vapor, and nitrogen oxides. And, radioactive / non-radioactive solid particles and volatile materials are also included in the off-gas. To reduce the radioactive contents in the off-gas to the level permissible to the atmosphere discharging, the melter is connected to the off-gas treatment system. The system also performs the function of maintaining the negative melter pressure. The off-gas treatment system used with TVF is shown in Figure 1.

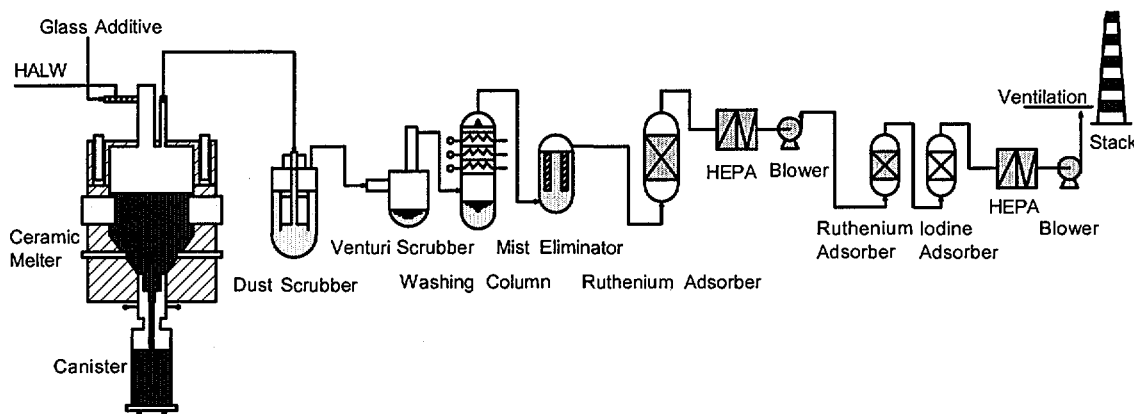


Figure 1. TVF Melter Off-gas Treatment System

The off-gas generated in the melter is first led to the dust scrubber through the off-gas pipe. In order to prevent the off-gas pipe plugging, there is the air-film cooler installed at the outlet of the melter. The configuration of the air-film cooler is shown in Figure 2. The off-gas film cooler consists of two concentric pipes forming an annulus. And, in the inner pipe there are several slits that direct the cooling air along the inner pipe wall in laminar flow. It is expected that the laminar flow prevents the particles from depositing on the surface of the off-gas pipe. On the other hand, the air-film cooler also helps to keep the off-gas temperature within the proper limits. The off-gas temperature changes depending

on the melter operating condition. If the off-gas temperature is too low, the boric acid vapor and the nitric acid vapor are easy to condense in the pipe. On the contrary, if the temperature is too high, the deposit in the pipe changes consistency to a “sticky” coating on the pipe surface. So, it is important to keep the off-gas temperature within the proper limits. After the off-gas is led to the dust scrubber, it is washed out, and the most particles are removed. Successively, it is led to the next off-gas treatment equipment.

At TVF, the rapid increased differential pressure between the melter plenum and the dust scrubber was experienced after radioactive operation using the actual waste had started. Once during non-radioactive test using simulated waste before radioactive operation, the differential pressure didn't increase so rapidly. And, it was maintained to be less than 250 mmH<sub>2</sub>O after 40 glass product bodies had been produced. However, during radioactive operation, the differential pressure exceeded 250 mmH<sub>2</sub>O before 20 glass product bodies had been produced. There is a spare pipe between melter and the dust scrubber. So, even though the off-gas pipe should be plugged, the off-gas could be drawn through a spare pipe. Therefore, the melter pressure can be maintained negative. However, it is desirable for stable melter operation to control the differential pressure less than 250 mmH<sub>2</sub>O. So, this phenomenon is harmful to the long-term continuous operation of the vitrification facility. The continuous operation is important particularly for the commercial vitrification facility. Therefore, the countermeasures were studied to suppress the increase of the different pressure, and to restore it.

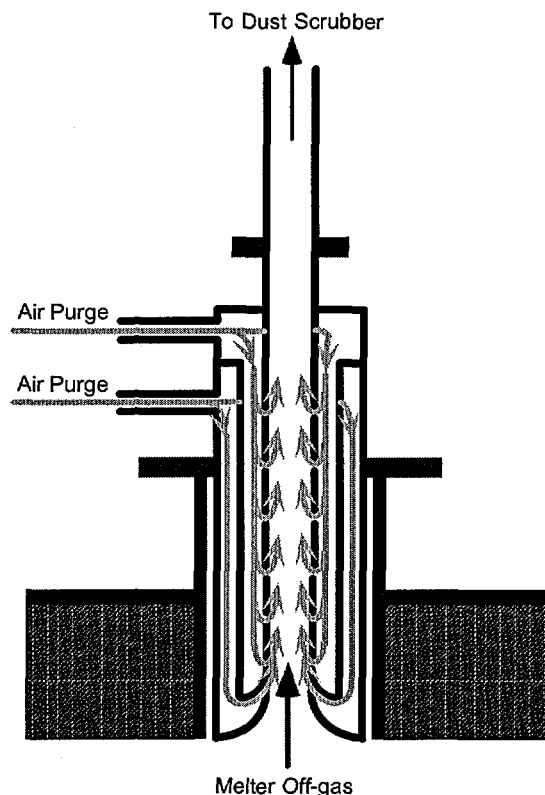


Figure 2. Configuration of Air-film Cooler

### STUDY ON DEPOSIT GROWING MECHANISM

To devise the countermeasures, it is important to find the cause of the increased differential pressure by the observation of the phenomenon. At first, the deposits sampled at the hot test operation of TVF were analyzed chemically. The result showed that the deposit is composed mainly of boron (B), sodium (Na), and Cesium (Cs). And, from the morphological observation, it was found that the deposits existed mainly around the slits of the air-film cooler, and that there were little deposits in the other location of the off-gas pipe. Further, it was known that the differential pressure restored by increasing the off-gas temperature. The transition of the differential pressure at the melter off-gas outlet pipe is shown in Figure 3. According to the chart, the rapid decreases take place at about 175°C, 200°C, and 240°C. The phase diagram for the system  $H_2O-B_2O_3$  is shown in Figure 4. The temperatures at which the rapid decreases take place were good coincident with the melting points of metaboric acids. In table 1, the physical properties of metaboric acids are summarized. The specific gravity of metaboric acid increases with the transformation ( $HBO_2III \rightarrow HBO_2II \rightarrow HBO_2I$ ). Therefore, the transformation of metaboric acid induces the deposit shrinkage. And, it can explain the restoration of the differential pressure at these temperatures well.

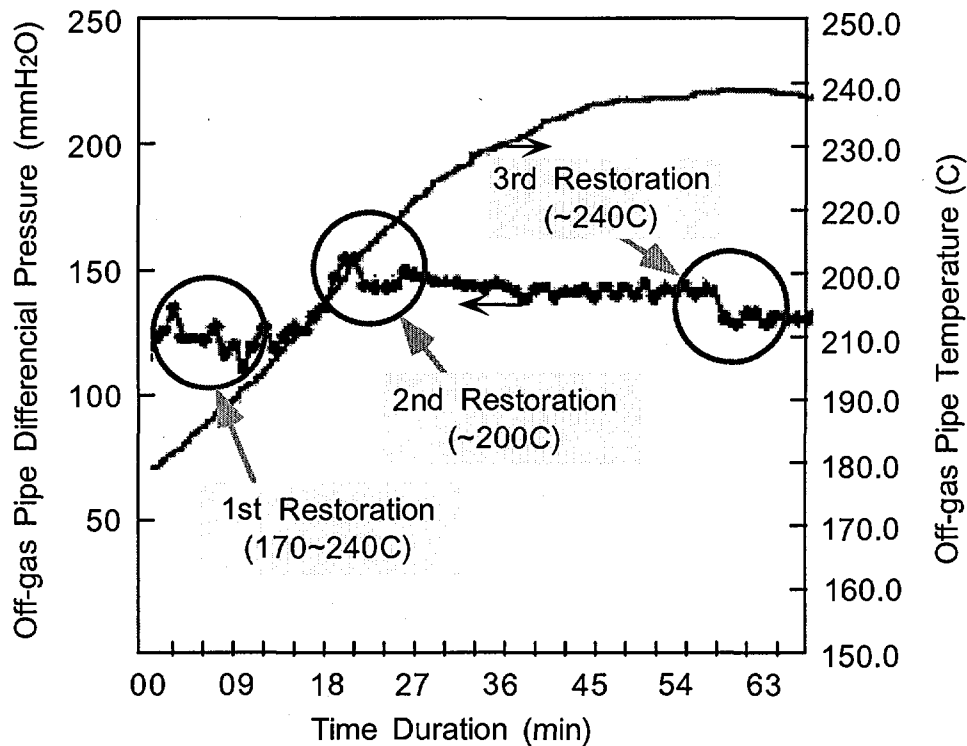


Figure 3. Transition of Differential Pressure at TVF Melter Off-gas Pipe

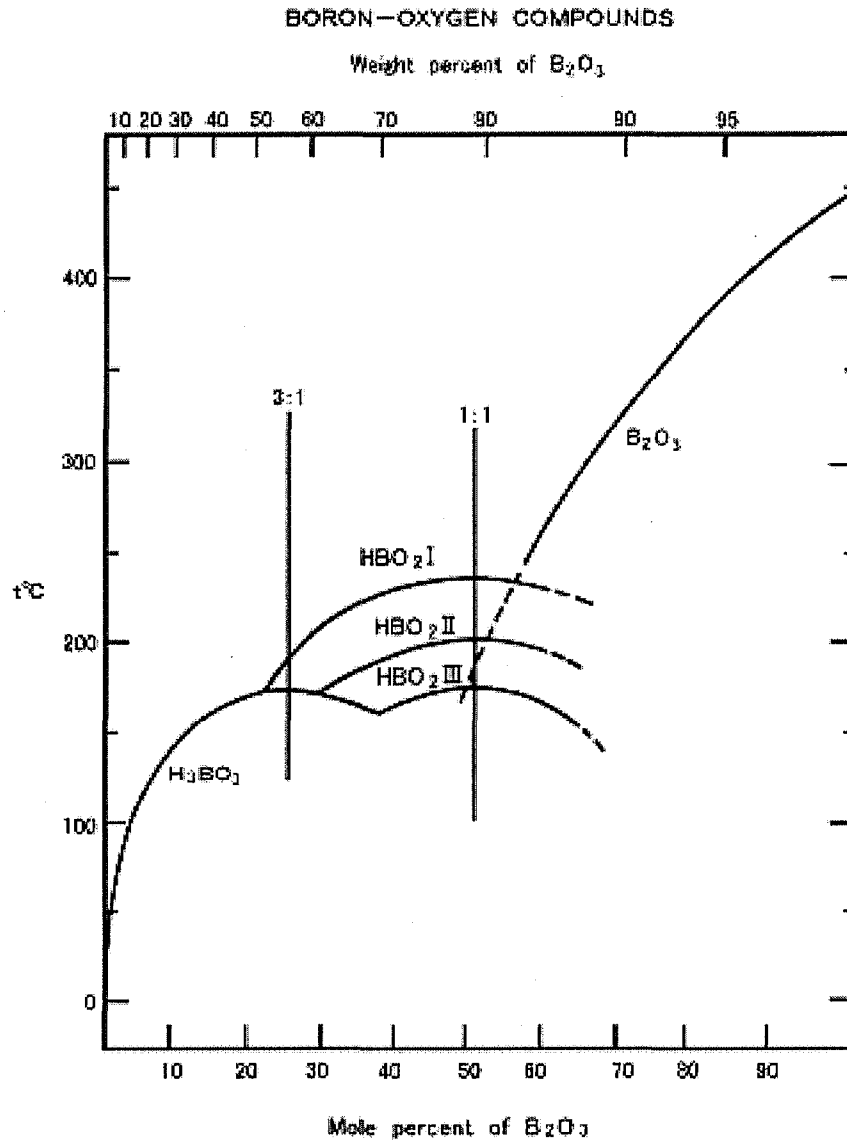


Figure 4. Phase Diagram for the System  $H_2O-B_2O_3$  [1]

Table 1. Properties of Boric Oxide System

	$B_2O_3$ Wt. %	Molecular Weight	Specific Vol. ( $cm^3/g$ )	Melting Point ( $^{\circ}C$ )
$H_3BO_3$	56.30	61.81	0.676	170.9
$HBO_2III$	79.45	43.81	0.561	176.0
$HBO_2II$	79.45	43.81	0.489	200.9
$HBO_2I$	79.45	43.81	0.402	236
$B_2O_3$	100.0	69.62	0.339	450

From the findings described above, It was presumed that the rapid increase of the differential pressure at the melter off-gas outlet pipe was attributed mainly to the deposit of metaboric acid that condenses at the outlet of the air-film cooler slits. Before the deposit growing mechanism is considered, it is necessary to know the vaporization properties of boric acid. According to Stackelberg's study [2] on the vaporization of boric acid with water vapor, the saturated vapor pressures of orthoboric acid and metaboric acid are represented by the following equations.

- Saturated Vapor Pressure on Orthoboric Acid Substance ( $P_{[H_3BO_3]}$ :mmHg)

$$\log P_{[H_3BO_3]} = 13.206 - \frac{5,125}{T} \text{-----} (1)$$

- Saturated Vapor Pressure on Metaboric Acid Substance ( $P_{[HBO_2]}$ :mmHg)

$$\log P_{[HBO_2]} = 2.627 + \log P_{H_2O} - \frac{1,950}{T} \text{-----} (2)$$

- Transformation Temperature from Orthoboric Acid to Metaboric Acid

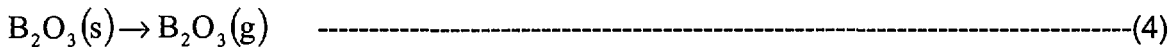
According to Stackelberg's study, the transformation temperature from orthoboric acid to metaboric acid depends on the water vapor pressure. The transformation temperature ( $T_u$ :°K) is obtained by the following equation.

$$\log P_{H_2O} = 10.579 - \frac{3,175}{T_u} \text{-----} (3)$$

Using equation (1),(2), and (3), the saturated vapor pressure of boric acid can be obtained under the certain water vapor pressure. Based on the vaporization properties of boric acid described above, the deposit growing mechanism is presumed as follows.

#### (1) Vaporization Process

The boron contains in glass material in the form of boron oxide  $B_2O_3$ . The boron oxide may be vaporized as follows.

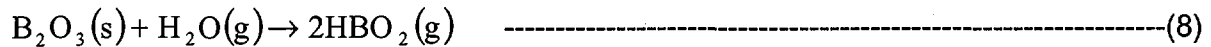
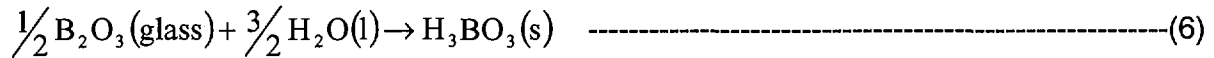


According to the reference, the vaporization pressure of the boron oxide can be represented by the following equation.

$$\log P = 9.624 - \frac{16,960}{T} \text{-----} (5)$$

( P : mmHg, T : °K )

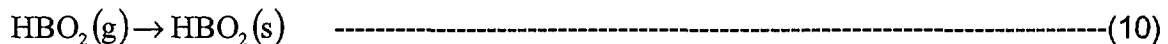
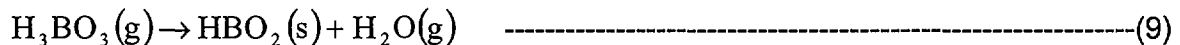
The temperature in the melter plenum is about 300 °C. At this temperature the vapor pressure of boron oxide is about  $10^{-20}$  mmHg. The trifling vapor pressure can not explain the plenty amount of boron gas generation. On the other hand,  $B_2O_3$  is known to react with  $H_2O$  to produce orthoboric acid ( $H_3BO_3$ ) and metaboric acid ( $HBO_2$ ). These reactions are expressed by the following equations.



Based on the mass-balance of the melter, the water vapor pressure in the melter plenum is estimated to be about 214 mmHg and the partial vapor pressure of boric acid in off-gas is about 0.2 mmHg. Using this water vapor pressure, the saturated vapor pressure of boric acid is evaluated in Figure 5. At 300 °C that is the typical temperature of the melter plenum in operation, the saturated boric acid vapor pressure is far higher than the partial vapor pressure of boric acid. Therefore, once boric acid is formed, it can be accompanied with melter off-gas easily.

## (2) Condensation Process

To clarify the reason why the deposit concentrates around the slits of the air-film cooler, the saturated vapor pressure of boric acid under the purge air condition is investigated. Since 0.7MPa compressed dry air is used for purge air, the water vapor pressure of the purge air is evaluated to be 2.6 mmHg. Using this water vapor pressure, the saturated vapor pressure of boric acid at the outlet of the air-film cooler is calculated and plotted in Figure 6. As known from the figure, the saturated vapor pressure is lower than the partial pressure of boric acid in off-gas under 250 °C. Therefore, if the purge air temperature is lower than 250 °C, the boric acid vapor should condense at the outlet of the slits. And, at 2.6 mmHg of water vapor pressure, metaboric acid is stable above 40 °C. So, it is also found that the stable chemical form of the condensed material is metaboric acid. The following reactions will occur around the slits of the air-film cooler.



As described above, the phenomenon can be explained by the assumption that boric acid generated in the melter condenses as the form of metaboric acid at the outlet of air purge slits.

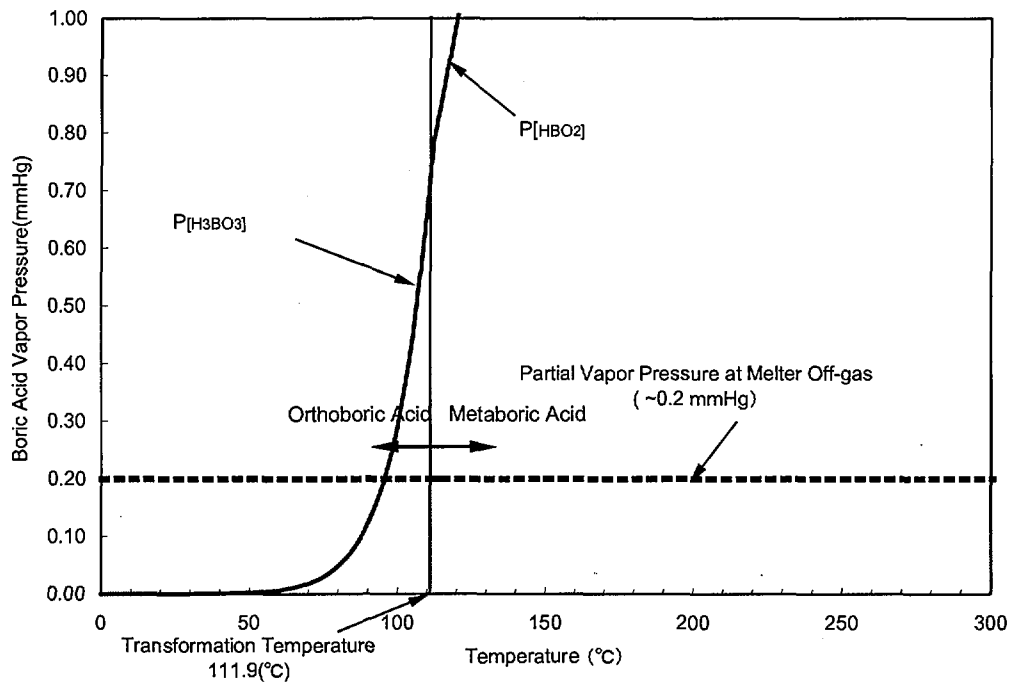


Figure 5. Boric Acid Vapor Pressure in the Melter Plenum  
(  $P_{H_2O} = 214 \text{ mmHg}$  )

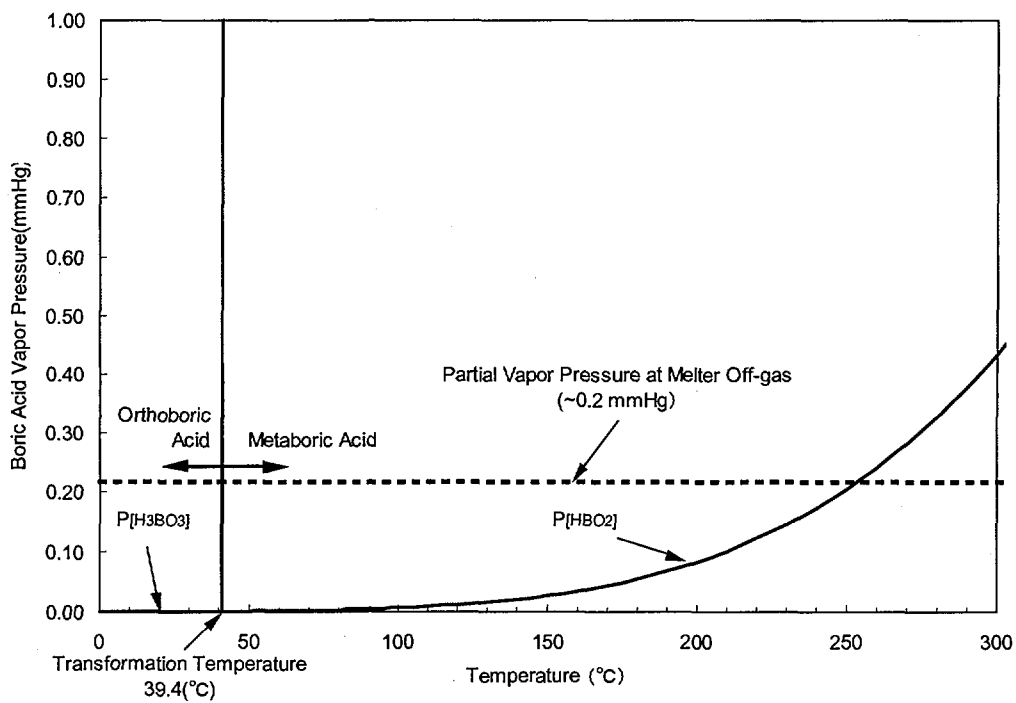


Figure 6. Boric Acid Vapor Pressure at the Outlet of Air-Film Cooler Slit  
(  $P_{H_2O} = 2.6 \text{ mmHg}$  )



## STUDY ON COUNTERMEASURES

In the study of the depositing mechanism, several countermeasures were considered to suppress the condensation of the boric acid at the outlet of the air-film cooler. Among them, it was thought that the heating and the humidification of purge air were the most effective methods. As described previously, the saturated vaporization pressure of boric acid is depending on both the temperature and the water vapor pressure. Figure 7. shows the diagram of the boric acid precipitation. In the diagram, the saturated vapor pressure of the boric acid is plotted as a function of the water vapor pressure. Line 1 is obtained by equation (2), and line 2 is obtained by equation (1). Here, if the operating condition exists in region A, metaboric acid ( $\text{HBO}_2$ ) condenses. And, in region B orthoboric ( $\text{H}_3\text{BO}_3$ ) acid condenses. In order to avoid the condensation, the operation condition should be in region C. The red dots shows the typical operating condition of TVF. The condition at the outlet of the air-film cooler exists in region A. If only heating is used, the temperature should be more than  $260^\circ\text{C}$ . However, if the humidification is used together, it is not necessary to heat up to so high temperature. For example, the temperature of  $120^\circ\text{C}$  is sufficient at 55.3 mmHg water vapor pressure, which is the saturated water vapor pressure at  $40^\circ\text{C}$ , 760mmHg. In order to avoid the deposit stick on the pipe wall, the lower temperature is preferable. Therefore, it is decided that both methods of heating and humidification are adopted for the commercial vitrification facility.

## WATER CLEANING SYSTEM

It seems to be difficult to avoid the deposit completely by the countermeasure of the heating and humidification of purge air. So, apart from them, another countermeasure to remove the deposits was studied. At the similar plants in the world, various methods were applied. These methods are classified into mechanical methods and hydrodynamic methods. After several kinds of mock-up tests, we concluded that the water cleaning system was the most effective methods to reduce the differential pressure without disturbing the melter operation. In Figure 8, the picture shows the acrylic model test. The objectives of the test were to investigate the optimum pipe configuration and the operating conditions for the water cleaning system visually. In the test, the simulated deposit was used, and the cleaning efficiency was evaluated changing the pipe configuration, the water injection nozzle location, the off-gas velocity, the water flow rate, and the washing periods. The washing water injected into the off-gas pipe forms annular flow along the inner surface. This shaking annular flow loosened up and dissolved the simulated deposits effectively, and flushed it from the off-gas pipe to the dust scrubber. Figure 9. shows the transition of the melter plenum pressure and the differential pressure between the melter plenum and the dust scrubber during the water cleaning operation. These fluctuations were so trivial. Thus, it was demonstrated that the water cleaning operation could be performed while that the melter was being fed without disruption of the melter operation.

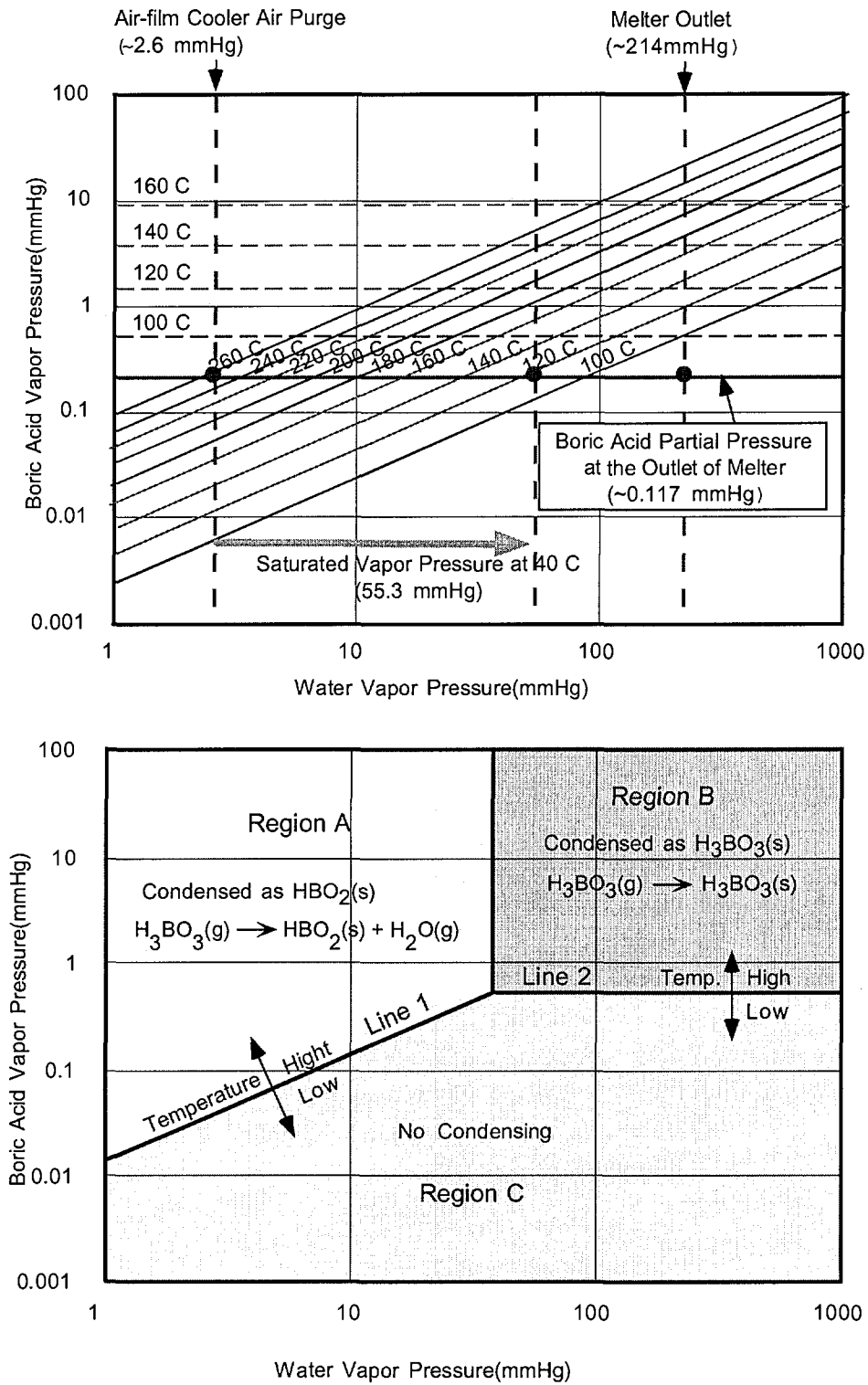


Figure 7. Boric Acid Precipitation Diagram

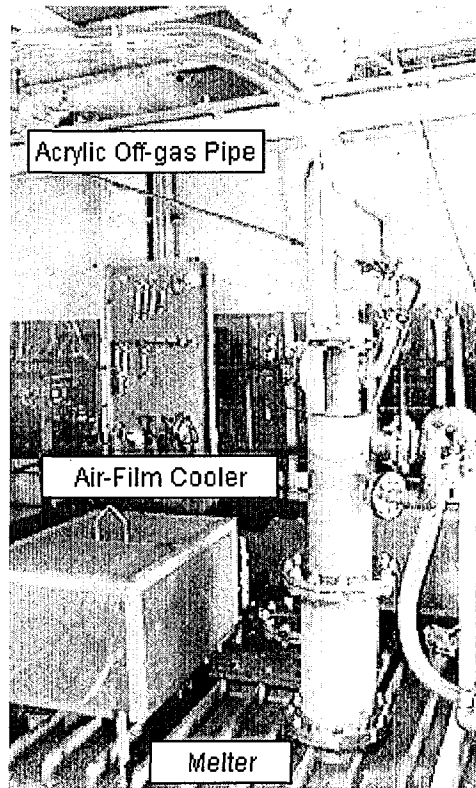


Figure 8. Acrylic Model Test

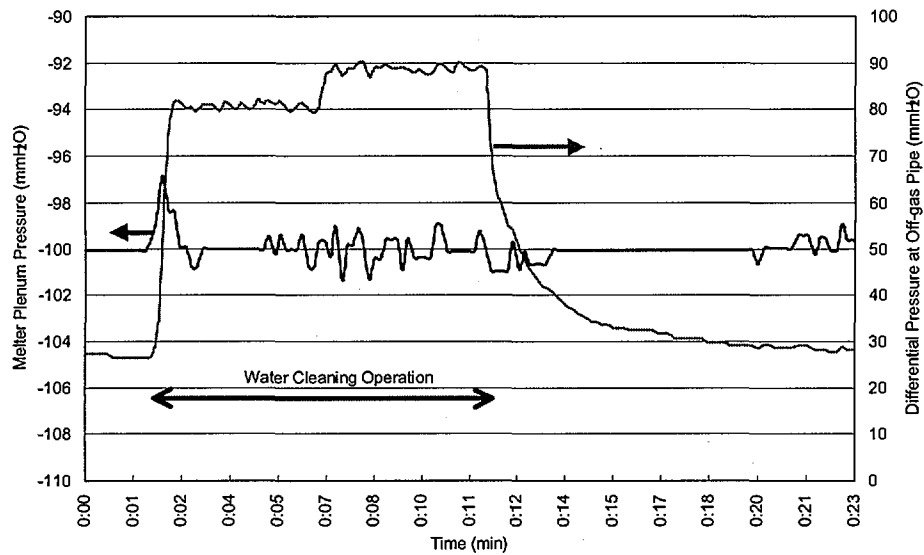


Figure 9. Transition of Melter Pressure and Off-gas Differential Pressure

## IMPROVEMENT OF OFF-GAS SYSTEM DESIGN

In order to ensure the long-term continuous operation, it was decided that the countermeasures developed were applied to the Japan's commercial reprocessing plant. The melter off-gas system was improved as shown in Figure 10. The purge air is heated to higher temperature and humidified out of the cell. And, it is supplied to the air-film cooler. Further, the two water injection lines are installed to supply the water to the air-film cooler and the off-gas pipe. The effectiveness of the system was also confirmed by the cold test using the commercial scale test melter.

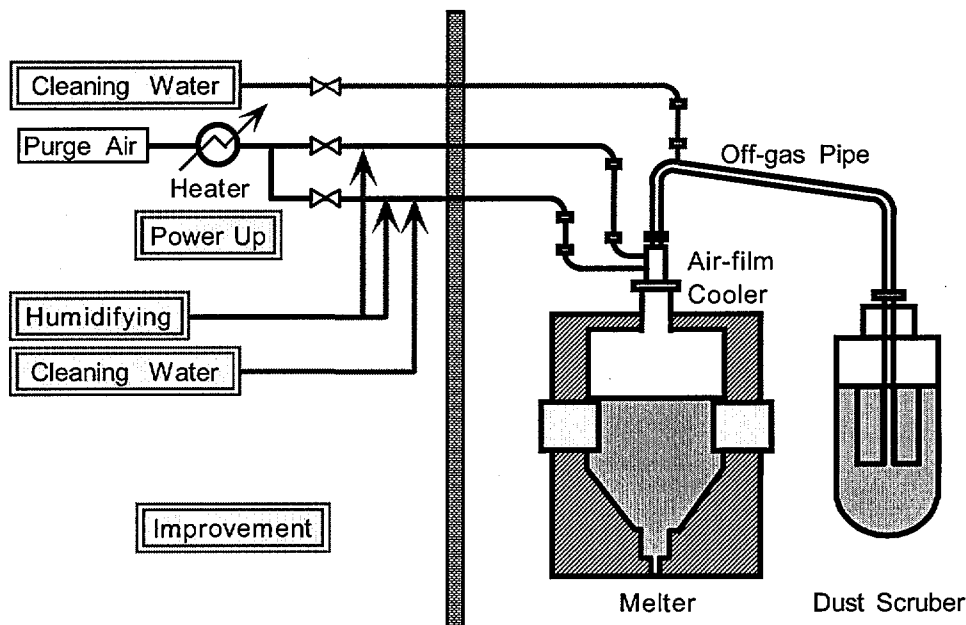


Figure 10. Improvement of Melter Off-gas System Design

## CONCLUSION

At the Tokai Vitrification Facility (TVF) that adopts the Liquid Fed Joule-Heated Ceramic Melter (LFCM), the rapid increase of the differential pressure between the melter plenum and the dust scrubber was observed during the radioactive operation. As this phenomenon was harmful to the long-term continuous operation, the countermeasures were studied and developed.

As the result of the survey, it was concluded that the phenomenon was attributed mainly to the condensation of metaboric acid at the outlet of the air-film cooler slits. Through the study on the deposit growing mechanism, the heating and the humidification of purge air were judged to be effective as the countermeasures to suppress the condensation. On the other hand, several countermeasures to restore the differential pressure were investigated as the provision against deposits. Among them, the water cleaning system that injects water into the air-film cooler and the melter off-gas pipe was evaluated to be the most effective and the most reliable methods.

In order to apply the system to the commercial scale plant, the scale-up tests were

conducted at JNC's mock-up facility using the acrylic model. As the result of the scale-up tests, the water cleaning system was also verified to be effective for the commercial scale melter. And, the optimum pipe configuration and the operating conditions were also evaluated.

As the final decision, it was determined that the heating and the humidification of purge air, and the water cleaning system were applied to the Japan's commercial vitrification facility, and the melter off-gas design was improved.

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