# Phase Diagram Study for the Alkali Metal-Oxychloride system

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Key Words: secondary fly ash, hot-filament method, oxide-chloride system

**Abstract**

Oxychloride systems are very important in the disposal of ashes generated from municipal wastes. The alkali metal-oxychloride system is a basic system of secondary fly ash generated in this process to reduce the volume of bottom ash and fly ash from incineration processes. Toxic materials such as compounds of heavy metals and dioxin may be absorbed by or contained in the secondary fly ash. In this study the phase stability of three binary systems was examined using a chemical equilibrium technique and a new hot filament technique, and a phase diagram for the NaCl-$Na_2CO_3$ system and liquidus for the NaCl-$Na_2SiO_3$ systems were obtained.

# I. Introduction

Most municipal waste in Japan is incinerated, and gas, bottom ash and fly ash are generated and processed as shown in Figure 1. Fly ash contains entrained particles and condensed vaporized metallic compounds trapped in dust chambers. Both bottom ash and fly ash are low in density so they must be reduced in volume for treatment at reasonable cost. These two types of ash are therefore mixed and melted to calcify them, but this process, in turn, generates secondary fly ash that contains heavy metals and chlorine.

Basic elements of the secondary fly ash are alkali metals, heavy metals, silicon, aluminum, calcium, chlorine and oxygen. The properties of these mixed oxychlorides is fundamental not only in the treatment of secondary fly ash but also in treatment of various other wastes. It is rarely found in the natural environment, only in artificial compounds, so very few studies have been made.

The objective of this work was to understand the thermodynamic nature of waste-generated oxychlorides, to make these materials nonpoisonous stock. As a first step, the liquidus of the sodium-silicon-chlorine-oxygen system was studied.

As a preliminary experiment, the $NaCl$-$Na_2CO_3$ system was examined by a hot filament technique. We measured the liquidus of the $NaCl$-$Na_2SiO_3$ system using a chemical equilibrium technique. A new method using the hot filament technique was developed for a sample with relatively high vapor pressure and the liquidus for the $NaCl$-$Na_2SiO_3$ and system was obtained. We thus verified the validity of results obtained by the hot filament and the chemical equilibrium techniques.

# II. Preliminary hot filament experiments

A schematic of the apparatus used in the hot filament technique is shown in Figure 2. A thermocouple (0.5mmϕ Pt-6% Rh/Pt-30%Rh) is used to hold the sample, to heat it and to measure the sample temperature all at the same time [1-3]. We placed the sample on the filament, changed the temperature and observed the state of the sample with an optical microscope; direct in situ observation was possible. The temperature was calibrated by measuring the known melting point of a pure substance such as $Na_2SO_4$, KBr, NaCl or $KNO_3$. The relationship between the temperature measured by the hot filament technique and reported melting points is linear.

The hot filament technique was used to examine the $NaCl$-$Na_2CO_3$ system. The mixture was placed on the filament and slowly heated in the hot filament cell. This cell was purged with argon gas to eliminate water vapor : the gas was introduced at a flow rate of 50 ml/min. First, we observed the solid phase (Figure 3 (a)), and then the solid-liquid phase (Figure 3(b)). We then observed the solid-liquid phases change to a complete single liquid phase (Figure 3 (c)). Samples were quenched for chemical analysis. Results obtained in this experiment are shown in Figure 4. Various compositions of this system were examined and the temperature at which the solid-liquid phase changed to the liquid phase (indicated by solid circles in Figure 4) was determined; the eutectic phase diagram obtained for this system is shown in Figure 4. In the sample with a component near the eutectic composition, the boundary between the solid and solid-liquid phases was observed. The eutectic temperature is measured and is shown by open circles. The data measured in this study are very close to those reported earlier [4], which are indicated by the dotted line. The hot filament technique makes in situ observation possible, and data we obtained using this technique can be one of the guidelines for the phase diagram. The accuracy of the measurements by the hot filament technique is mentioned in the previous study. [3]

# III. Measurement of liquidus for the NaCl-$Na_2SiO_3$ system by the encapsulated technique

## III.1. Experimental

The vapor pressure of alkali metal chloride is relatively high so that the usual chemical equilibrium technique cannot be used, because the composition of the sample varies during the experiment with the evaporation of certain components. In this study, we encapsulated the sample in a closed end nickel tubing to avoid evaporation loss.

The liquidus saturated with $Na_2SiO_3$ was measured by equilibrating liquid phase and solid $Na_2SiO_3$ in the closed end nickel container. $Na_2CO_3$ and $SiO_2$ were carefully weighed and thoroughly mixed, put into a Pt crucible and melted in a furnace at about 1273K under dry Ar atmosphere for 45 minutes then the conglomeration of $Na_2SiO_3$ was required. 0.9g of this $Na_2SiO_3$ and 0.3g of powdery NaCl was sealed into the nickel tube. The specimen was then enclosed in the tube by welding the nickel tube. These samples were kept in a furnace for a given time at a given temperature, then quenched in water with ice. The nickel tube was opened, the formerly liquid phase and conglomeration of $Na_2SiO_3$ were distinguished from their structural characteristics. This formerly liquid phase was separated, and its composition was determined by analyzing Si composition in this phase using inductively coupled plasma emission spectrometry (ICP).

## III.2. Results and Discussion

Dependence of compositions in the liquid phase on experimental time at 1173K is measured. $Na_2SiO_3$ increased with time and saturated at 85mol% after 24 hours; for safety we fixed the experimental time as 40 hours.

The experimental results of the liquidus composition saturated with $Na_2SiO_3$ are plotted in Figure 5 as open circles. The liquidus composition shifted to higher $Na_2SiO_3$ as temperature increased.

The chemical equilibrium technique is reliable and widely used, and the results are dependable. In this study, we obtained the liquidus by encapsulating the specimen. These liquidus are first reported.

# IV. Continuous evaporating hot filament technique

## IV.1. Experimental

The vapor pressure of many alkali metal chlorides are about $10^{-4}$Pa above 1000K, making it difficult to use the conventional hot filament technique as mentioned earlier; thus a new technique was used in this study. We transformed the filament as shown in Figure 6. NaCl held at the section of the filament was kept at a temperature above the melting point of NaCl. The sample was quenched by putting $Na_2SiO_3$ prepared as stated above on the molten NaCl and shutting down the heating power with a controller. This created a block in which NaCl and $Na_2SiO_3$ coexisted. We held this sample at a given temperature and observed its melting characteristics. We then quenched the sample by shutting down the heating power by a controller, and the liquid phase was separated mechanically, then chemically analyzed for Si composition using ICP and Cl by ion-exchange chromatography.

## IV.2. Results and Discussion

A sample in which NaCl and $Na_2SiO_3$ coexisted was placed on a section of the filament (Figure 7 (a)). Temperature was then kept above the melting point of NaCl (Figure 7 (b)). The vapor pressure of NaCl was relatively high in this system so that this compound in the liquid phase gradually evaporated. $Na_2SiO_3$ was dissolving in the liquid phase at the same time, so that the concentration of $Na_2SiO_3$ in liquid phase increased as the NaCl evaporated (Figure 7 (b)). Finally, the change of the state of the solid phase was observed. This liquid was saturated

with $Na_2SiO_3$ solid phase, and reached equilibrium in about 1.5h. The sample was quenched and composition of the liquid phase was analyzed. Results are shown in Figure 5 by filled circles. Figure 5 shows the curve of the liquidus of the NaCl-$Na_2SiO_3$ systems acquired in this study.
The new applied hot filament technique: continuous evaporating hot filament technique and the encapsulation technique were developed to obtain the liquidus.
In Figure 5, closed circles show the liquidus for the NaCl-$Na_2SiO_3$ system measured by the new appl.ied hot filament technique and open circles show that by the chemical equilibrium technique. A good agreement is seen between the results.
It is clear that the new hot filament technique is very simple and requires only a small amount of sample, as well as being reliable for making a phase diagram.
In the preliminary experiments, our results agreed well with those published eutectic phase diagram. And Figure 8 shows the phase relation for the NaF-$Na_2SiO_3$ system reported by Willgallis[5]. Liquidus for the NaCl-$Na_2SiO_3$ system in the region above about 50 mol% of silicate is overlayed on the same figure. These systems differ from each other in one factor: F and Cl, both are halogen elements. From these, we presumed that the NaCl-$Na_2SiO_3$ system may be a eutectic system as indicated by dotted line in Figure 8. However there are some uncertainties and needs further experimental consideration.

## SUMMARY

1. Phase diagram data for the NaCl-$Na_2CO_3$ was obtained using in situ observation of a hot filament. Results were very close to those in the literature. This system has eutectic composition at about 43mol% $Na_2CO_3$, and the eutectic temperature is 916K.
2. The liquidus for the NaCl-$Na_2SiO_3$ system was measured by the equilibrium technique for an encapsulated specimen and by the applied hot filament technique. There was good agreement between the results.
3. Liquidus for both the NaCl-$Na_2SiO_3$ systems using the applied hot filament technique increased with increasing mole fraction of silicate in the region above about 50%. Data of low silicate compositions did not clearly indicate phase relations there.

## ACKNOWLEDGEMENTS

The authors wish to thank Prof. A. Pelton of École polytechnique de Montréal and Prof. T. Nakamura of Tohoku University who offered valuable advice.
Mr. T. Namekawa of the machine shop of IIS, The University of Tokyo, was helpful in preparing the experimental apparatus.

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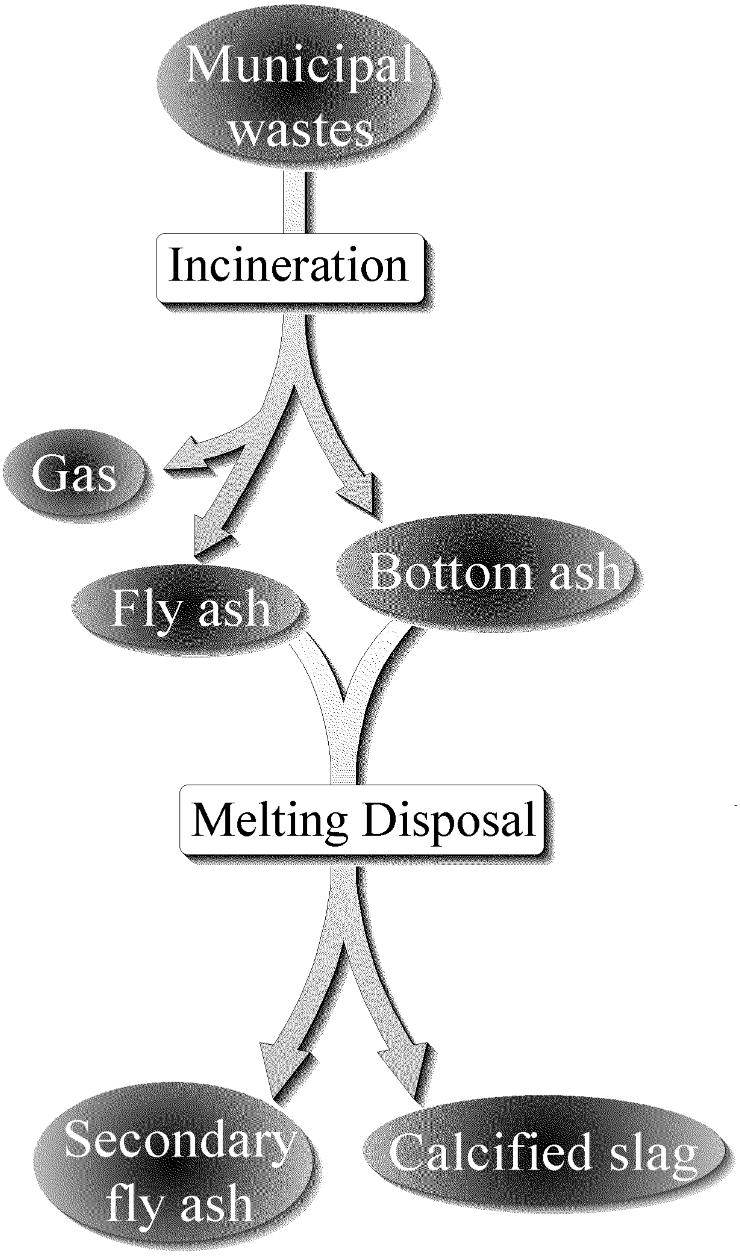


Figure 1: Ashes generated in various processes during incineration of municipal wastes.

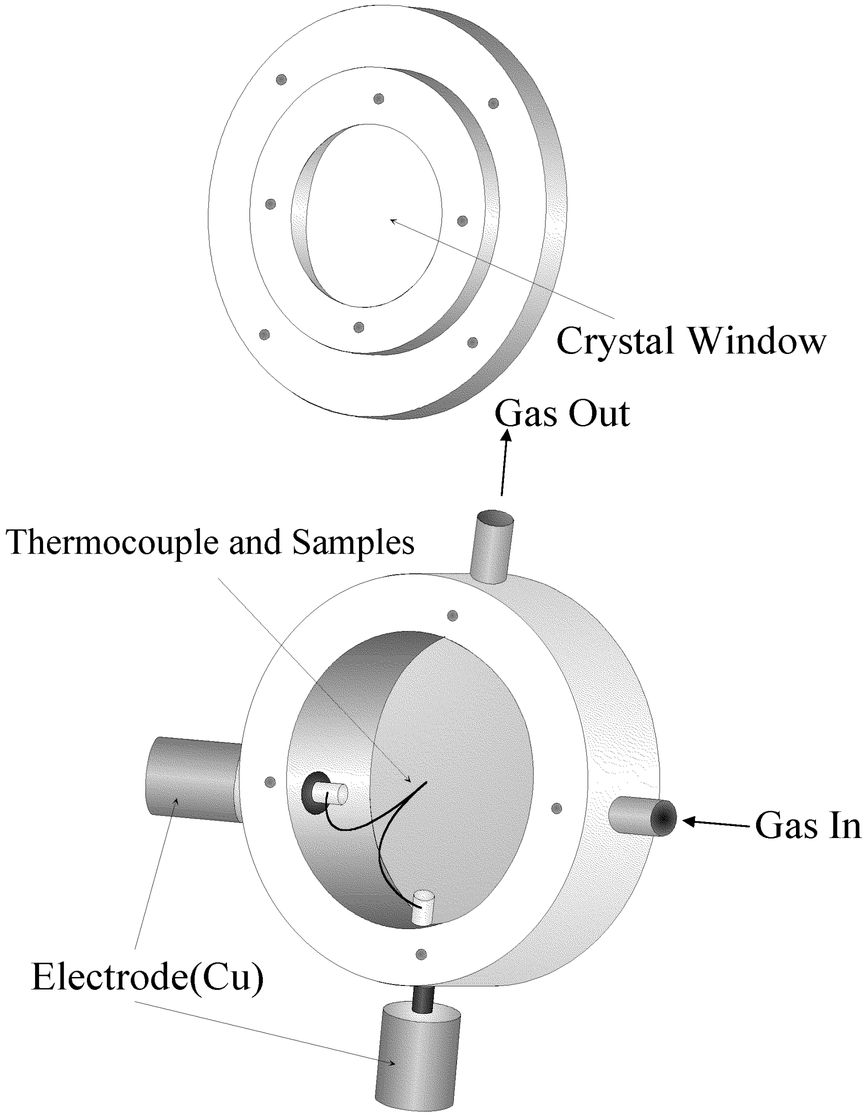

Figure 2: Schematic of a cell used in a hot filament technique.

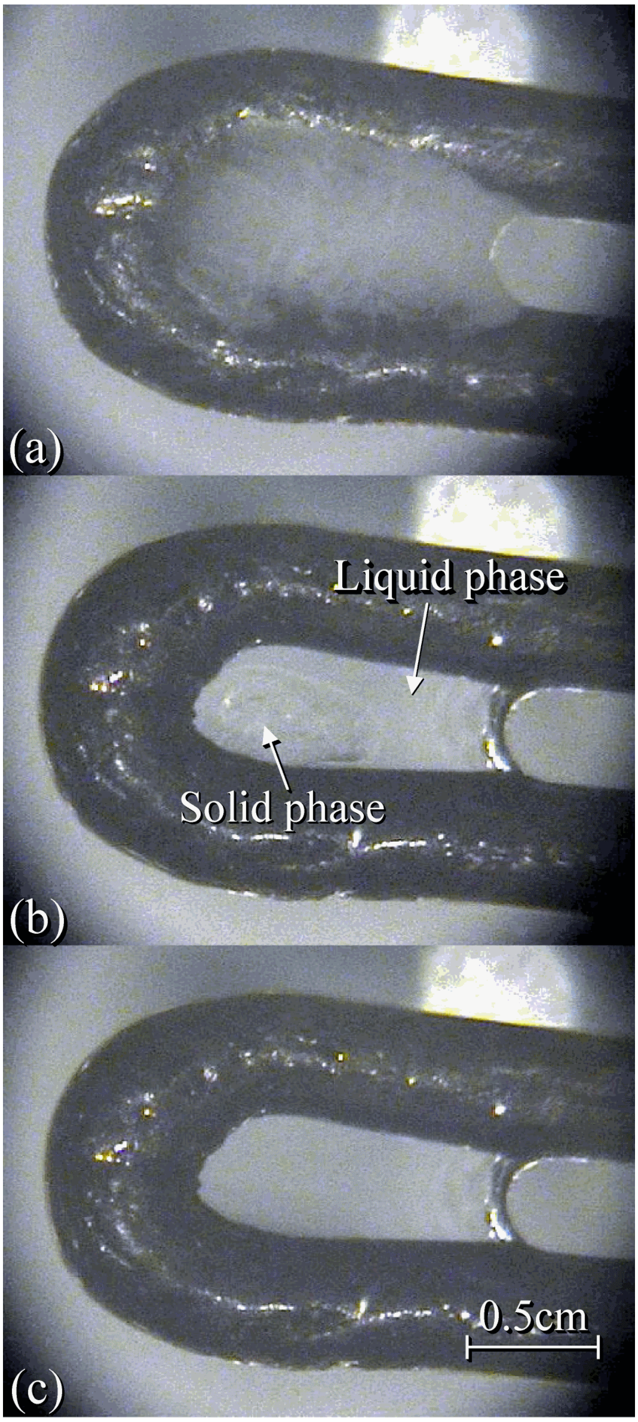


Figure 3: Observation of solid-liquid phase and liquid phase on hot filament.

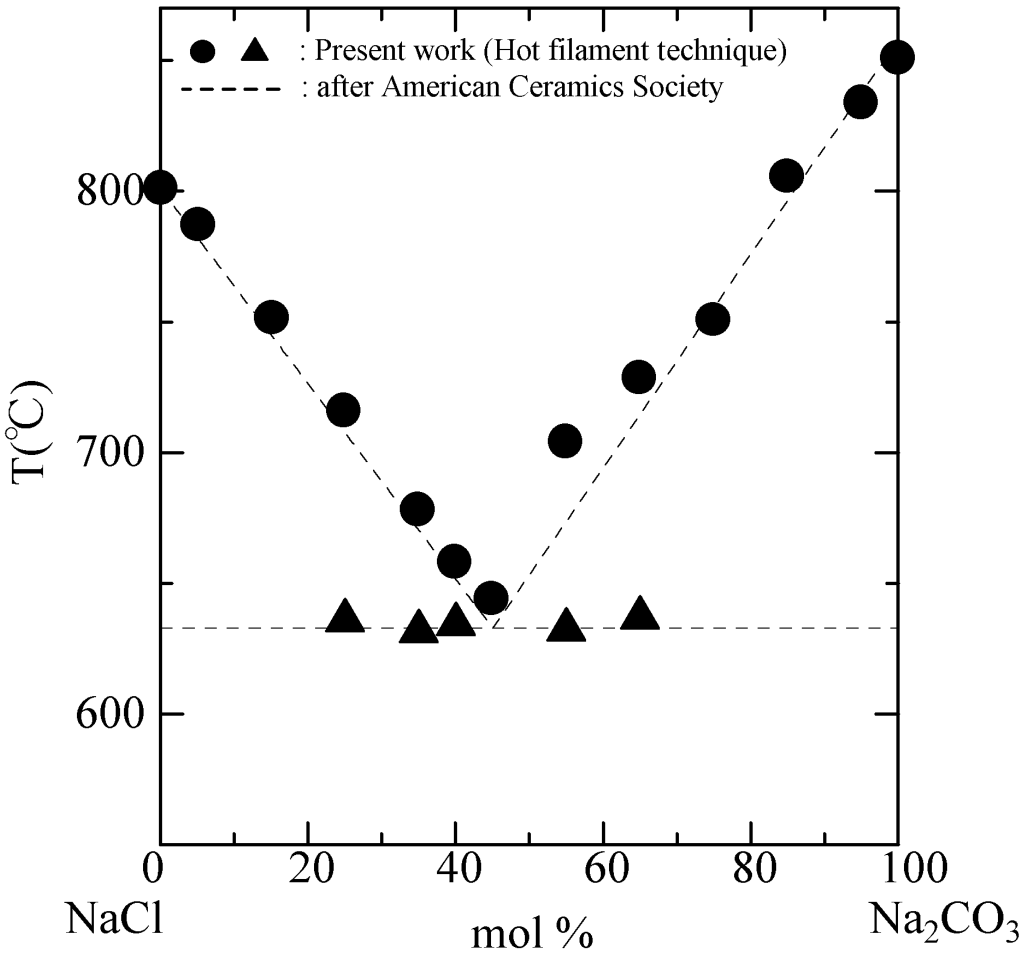


Figure 4: Phase diagram for the NaCl-$Na_2CO_3$ system.

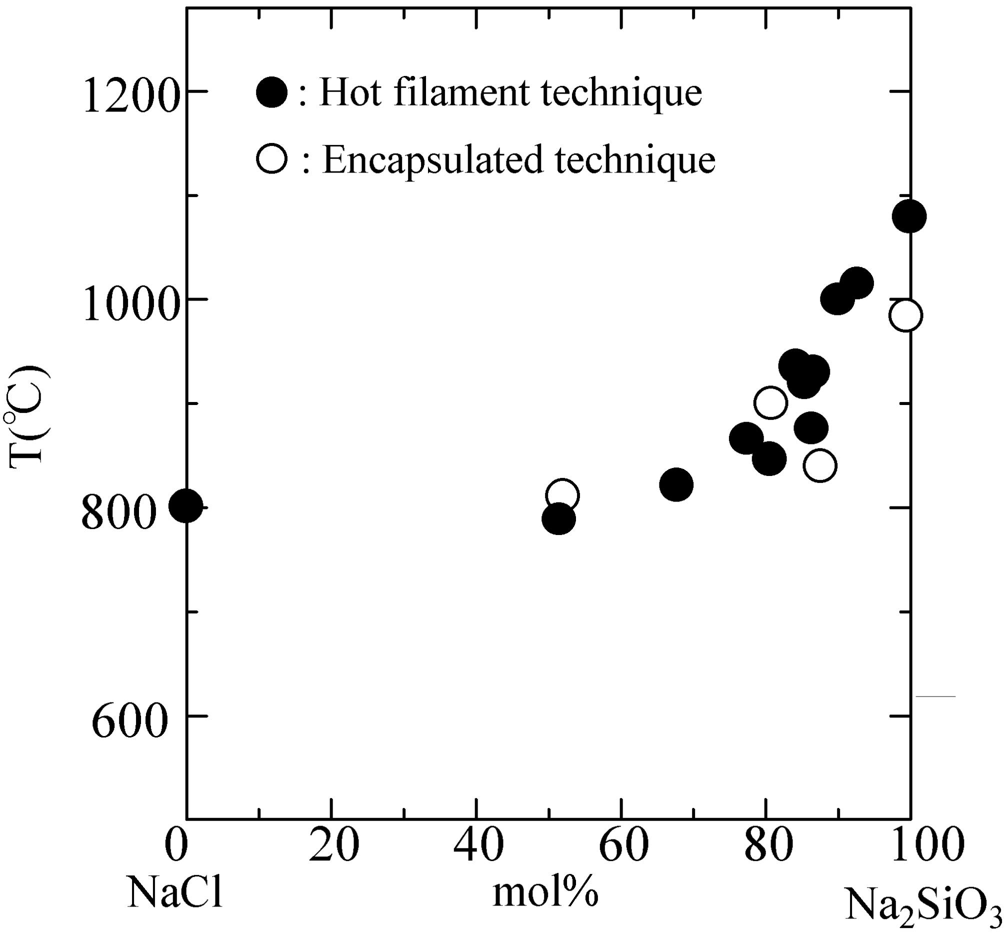


Figure 5: Phase diagram for the NaCl-$Na_2SiO_3$ system.

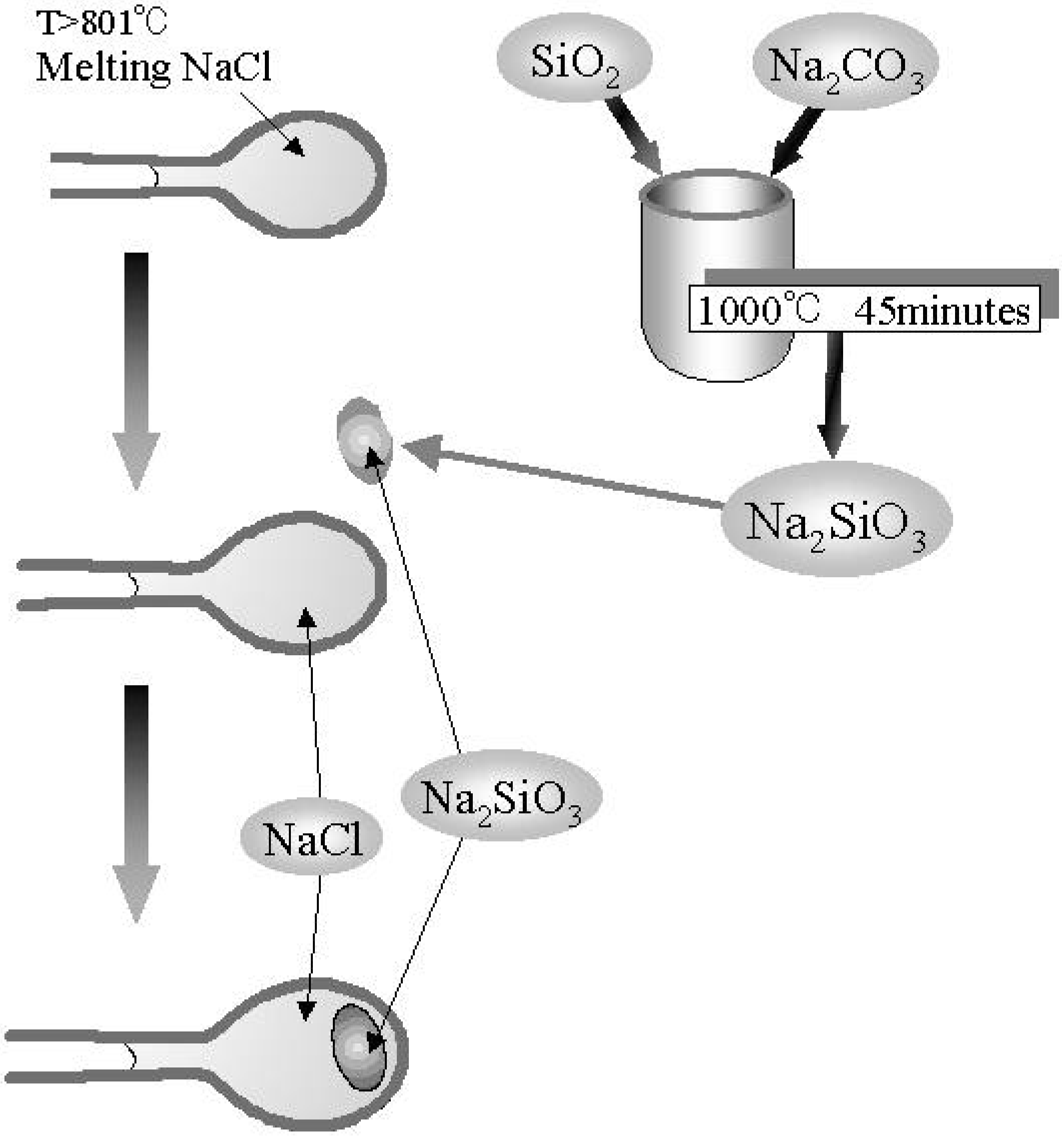


Figure 6: Preparation of the block in which NaCl and $Na_2SiO_3$ coexisted.

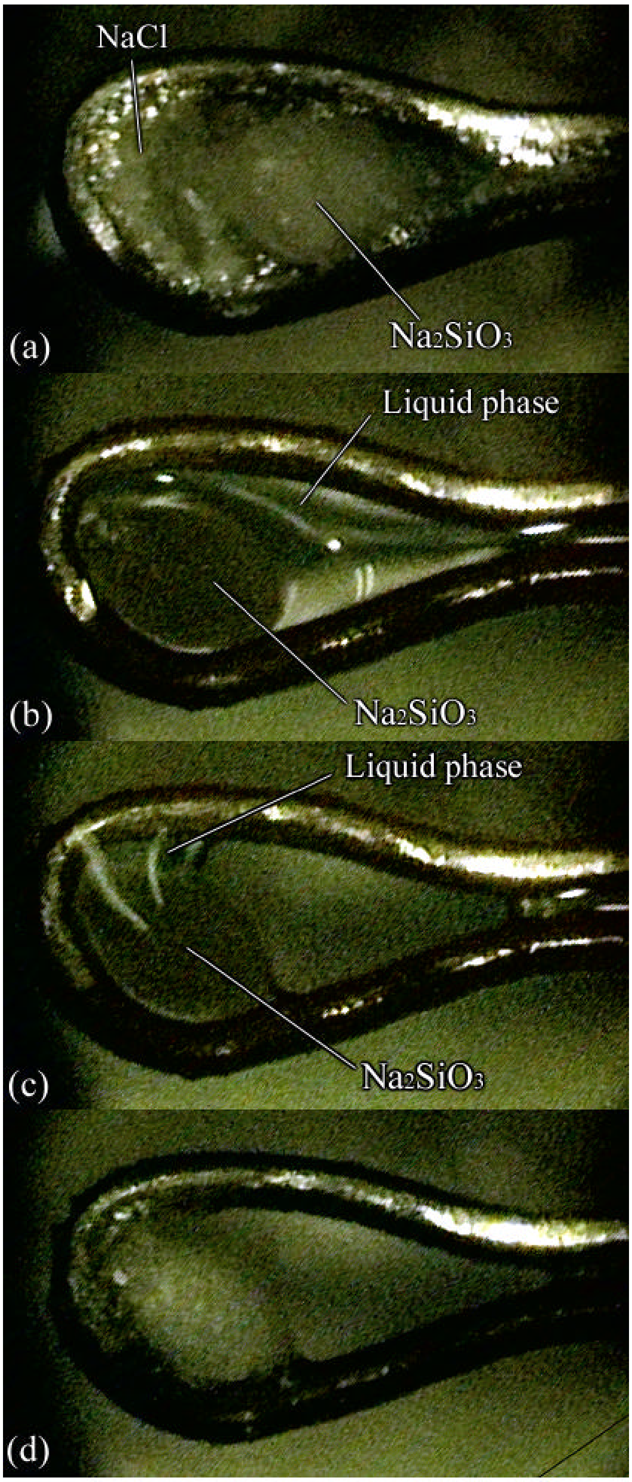


Figure 7: Observation of liquidus on hot filament.

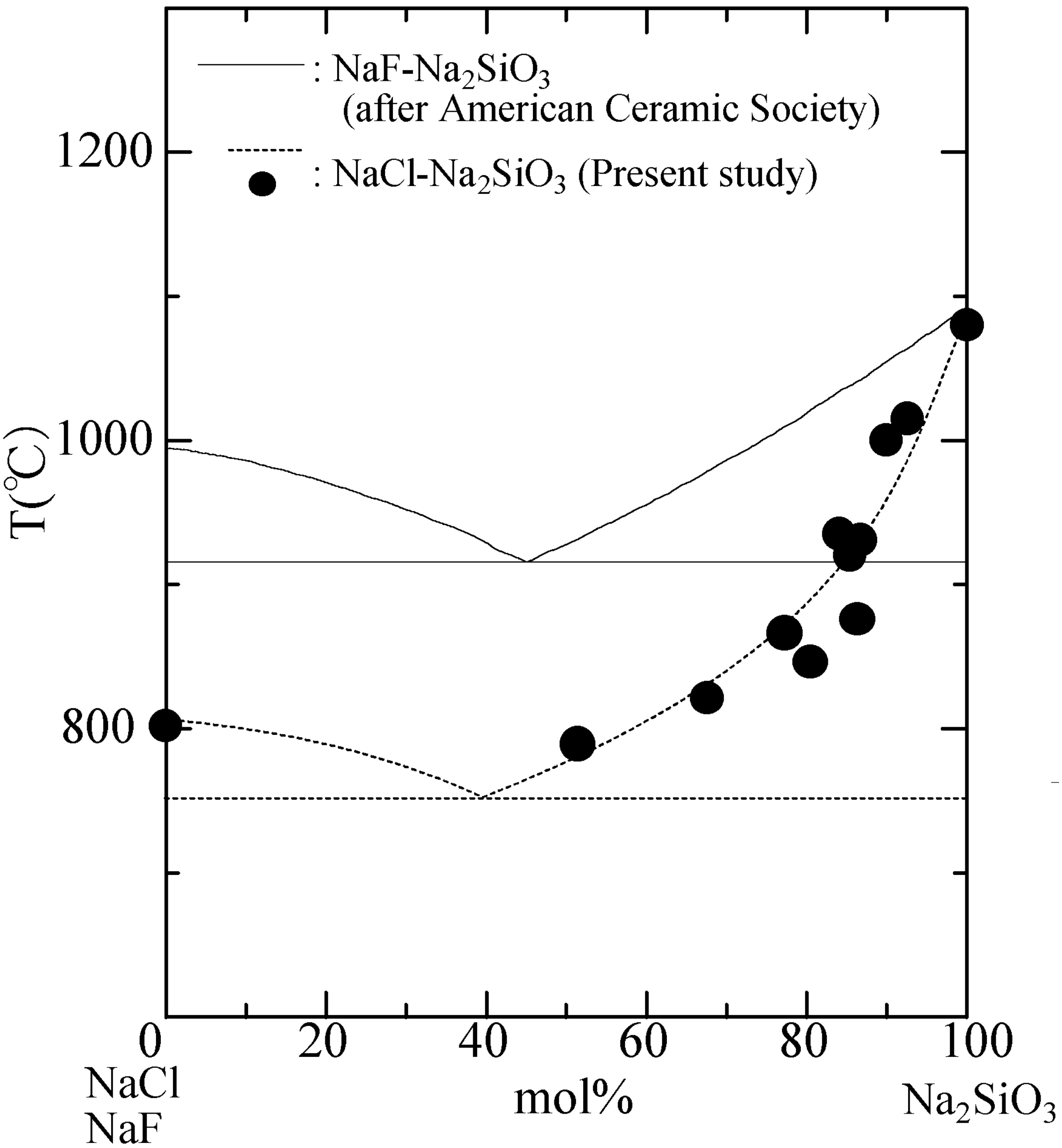


Figure 8: Phase diagram for the sodium halogen-sodium silicate system.