Chapter IV

Results and Discussion

4.1 <u>Resistivity measurement</u>

4.1.1 One component

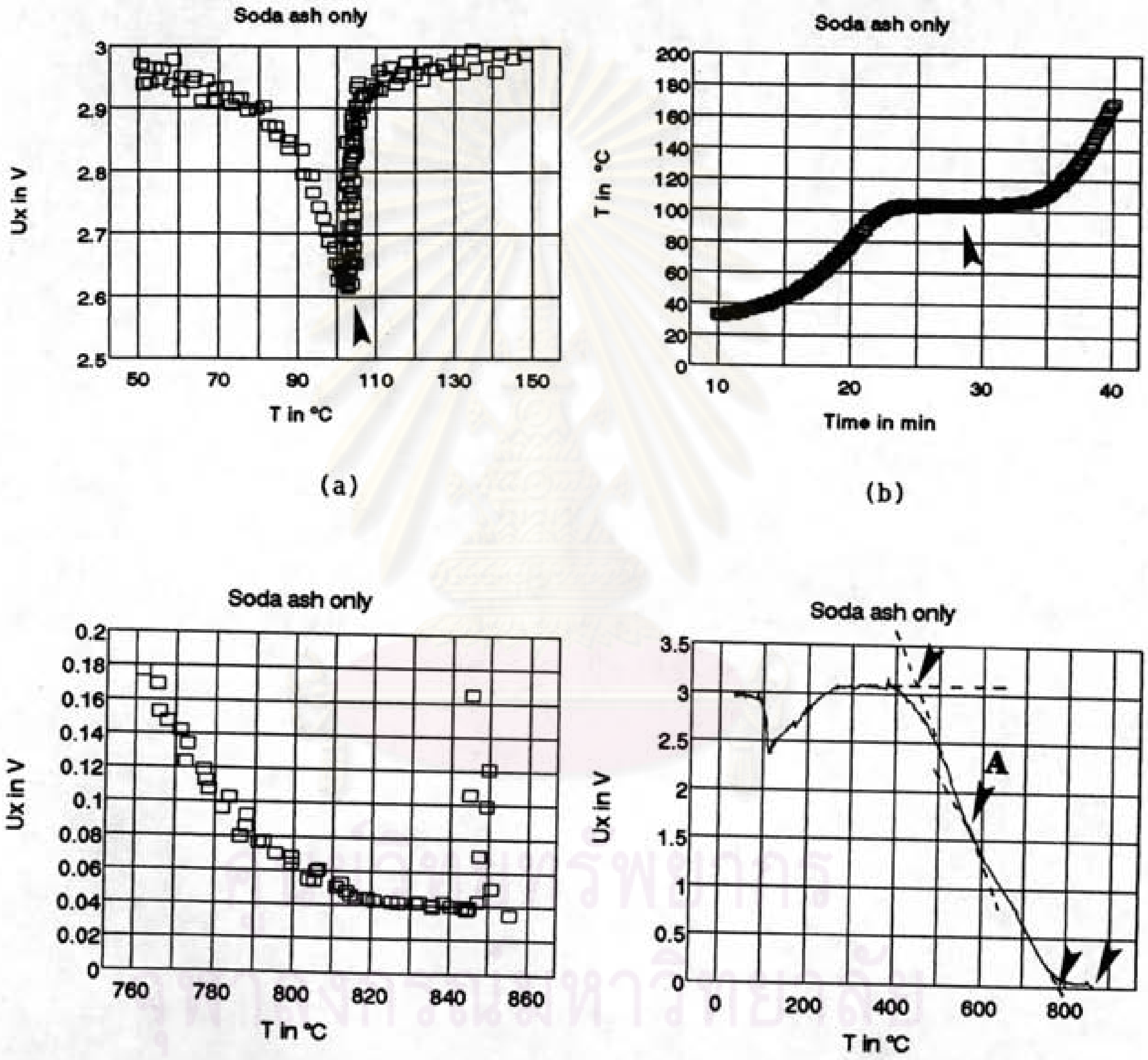
Resistivity measurements on one-component systems are shown in the following figures. They indicate that liquid phases are not formed in the system of sand, limestone and dolomite. However, distinct thermal effects clearly document the one-step decay of limestone at 900 ^{o}C, and the two-step decay of dolomite at approx. 700 ^{o}C and 900 ^{o}C. The first system discussed is Na_2CO_3 (fig. 4.1).

Soda ash

Figure 4.1 shows two main events which occur with soda ash. Figure (a) and (b) show that the resistivity decreases at a temperature of 104 to 106 ^{o}C, and the temperature remains constant at this level for 12 min. This is a clear indication of the dehydration reaction

$$Na_2CO_3.H_2O \text{ -----> } Na_2CO_3 + H_2O,$$

see also the phase diagram in figure 4.2. At a temperature of ~ 360 ^{o}C, the resistivity start to decrease again due to increase alkali ion mobility. A cross-over occurs at a temperature ~ 720 ^{o}C. The resistivity shows a change of slope (A), which a polymorphic inversion of soda ash (460 ^{O}C Speyer 1993, 450 ^{O}C Alcock 1993). Finally, soda ash (i.e, our specific industrial grade quality) melts at 850 ^{O}C; see figure 4.1.(c).



(a) (b)

(c) (d)

Figure 4.1 Low-T behavior of soda ash a) voltage indicating electrical resistivity, as a function of temperature, b) temperature , as a function of time, c) melting of soda ash as indicated by resistivity drop, d) overall resistivity.(same test as c.)

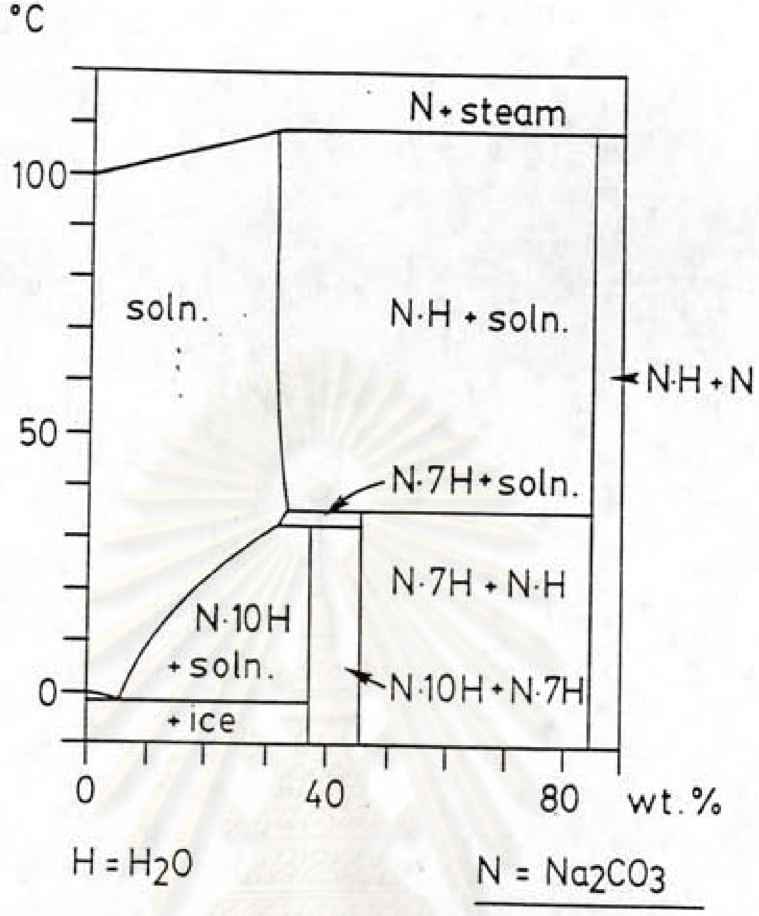
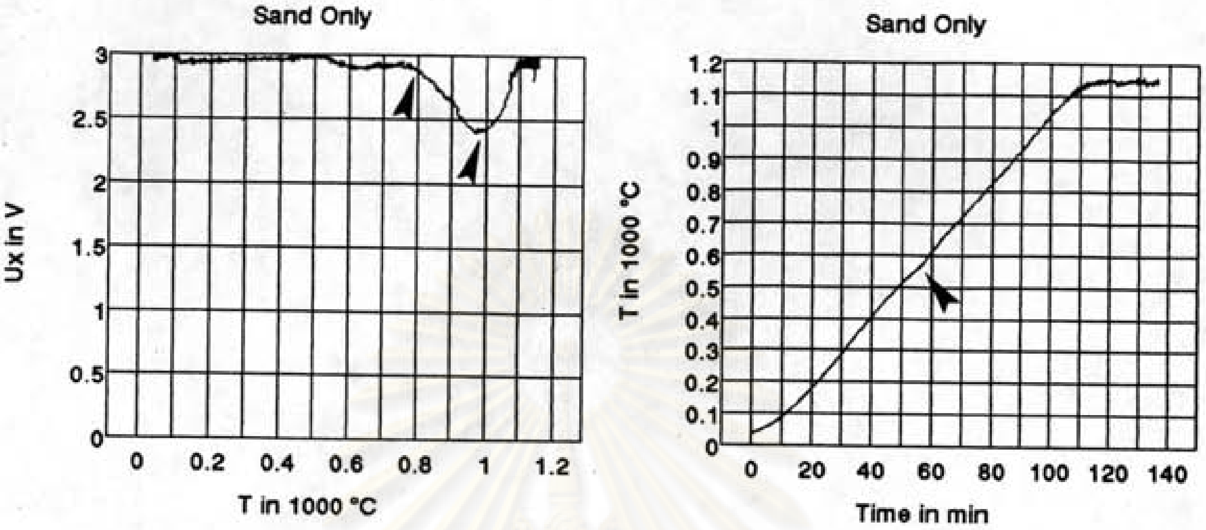


Figure 4.2 Phase diagram of Na_2CO_3-H_2O system, after Firma Henkel, Dusseldorf.

Sand

The resistivity of sand is constant until 800 °C it begins to decrease, passes through a minimum at approx. 1000 °C, then increases again. This behavior was rechecked and confirmed (see figure 4.4). The effect cannot be related to any distinct event without hesitating. It should be mentioned that high-T quartz becomes unstable with respect to high-T tridymite at 867 °C, and with respect to high-T cristobalite at 1025 °C. Alternatively, feldspatic impurities might lead to (spatially very limited) eutectic melting at approx. 1000 °C. Thermal effects (figure. 4.3 b) are not found, except for the well-known low/high-T quartz conversion.



(a) (b)

Figure 4.3 High-T behavior of sand a) resistivity. b) batch temprature.

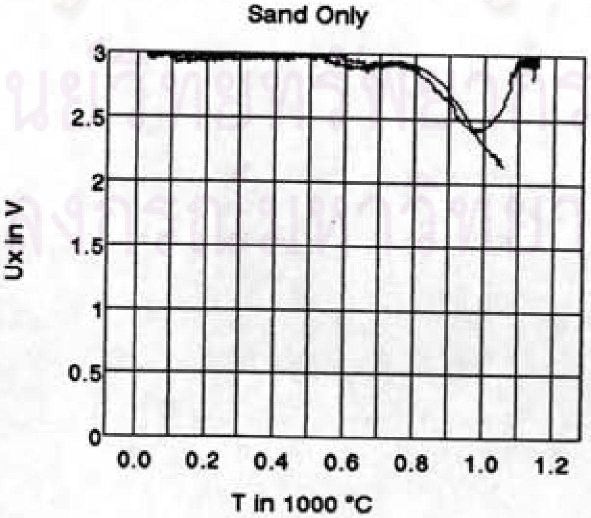
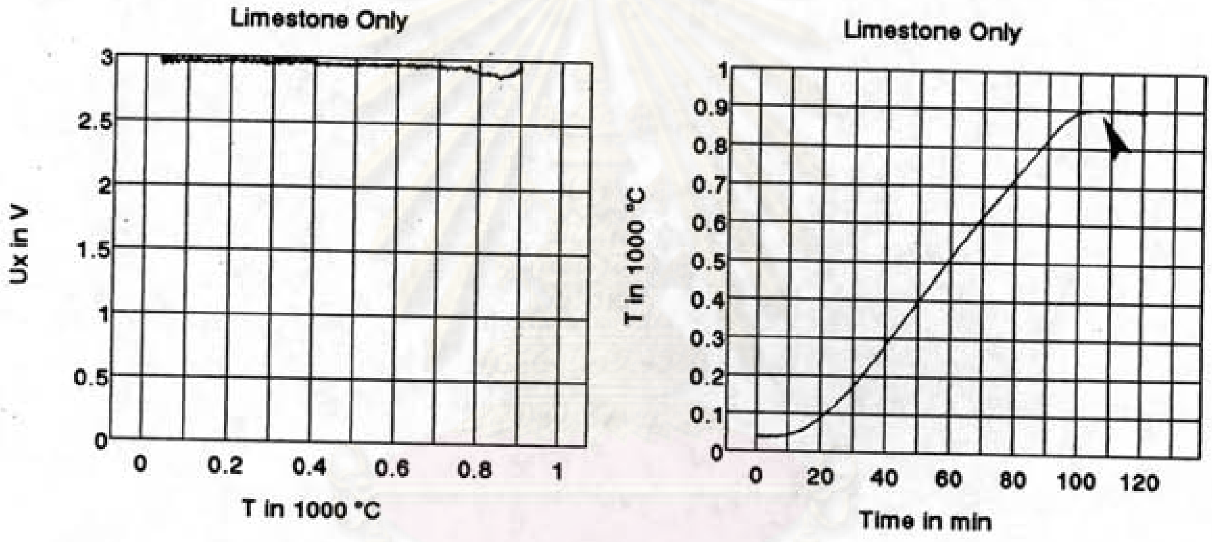


Figure 4.4 High-T behavior of sand double test.

Limestone

The resistivity of limestone is constant from room temperature to 1190 ^{o}C. A small hump at ~ 850 ^{o}C can be detected. The batch temperature remains constant at ~ 900 ^{o}C (see figure 4.5) because of the decomposition reaction:

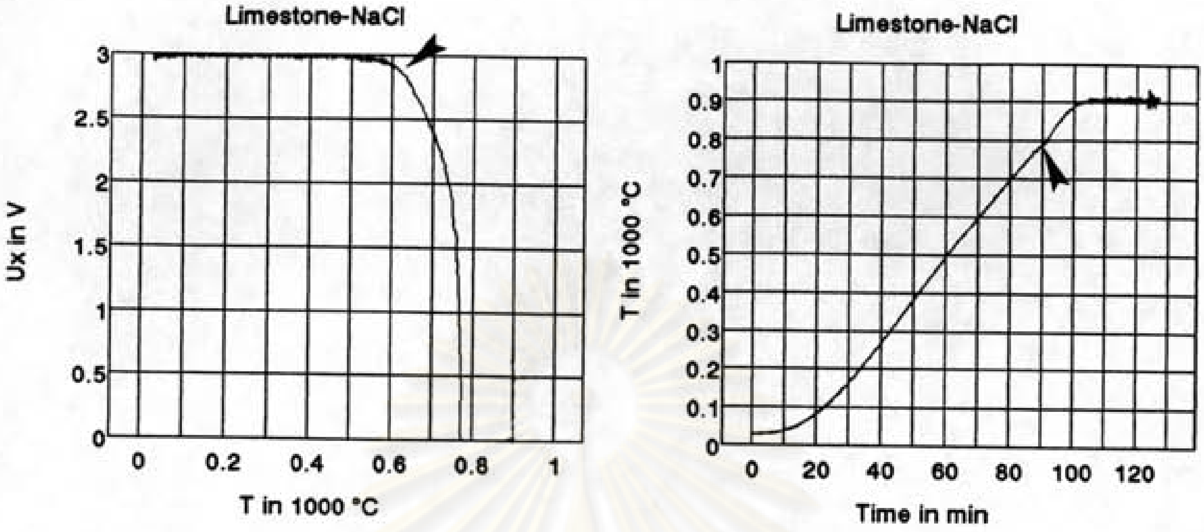
$$CaCO_3 \text{ -----> } CaO + CO_2$$



(a) (b)

Figure 4.5 High-t behavior of limestone a) resistivity. b) batch temperature.

Further studies of limestone refer to its interaction with NaCl. Figure 4.6. shows the results of limestone with 5 wt. % NaCl. It shows that the resistivity starts to decrease at 610 ^{o}C. The slow decrease of resistivity in the first region until 700 ^{o}C, is followed a sudden drop to zero at 783 ^{o}C. The batch temperature shows a small yet remarkable endotherm at 790 ^{o}C. An earlier phase diagram presents a eutectic $NaCl-CaCO_3$ at 789 ^{o}C, 6 wt. % $CaCO_3$.



(a) (b)

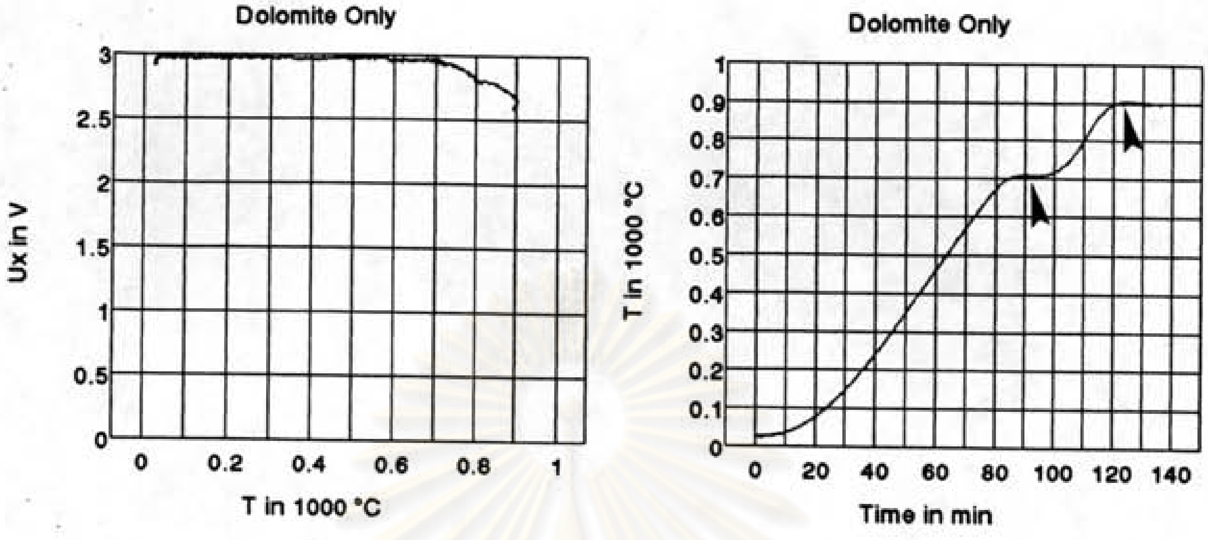
Figure 4.6 High-T behavior of lime with 5% NaCl a) resistivity, b)batch temperature

Dolomite

From the result in figure 4.7, the resistivity is constant from room temperature up to 700 ^{o}C. After that, it starts to decrease slightly. The batch temperature is steady at 2 levels, at temperature of 720 ^{o}C and 900 ^{o}C. (see figure 4.7 b). This can be described to a two-stage reaction. Firstly, dolomite decomposes to magnesium oxide and calcium carbonate. Secondly, calcium carbonate decays:

$$CaMg(CO_3)_2 \text{ ---------> } MgO + CaCO_3 + CO_2$$

$$CaCO_3 \text{ ---------> } CaO + CO_2$$



(a) (b)

Figure 4.7 High-T behavior of dolomite. a) resistivity, b) batch temperature

4.1.2 Two components

Soda-sand system

Soda ash (size as received from Bangkok Glass Co.,Ltd.) was mixed with 4 different sizes of sand described as coarse (1.000-2.000mm), medium (0.350-0.500mm), fine (0.185-0.250mm) and flint (<0.063mm). The results of resistivity measurement are compared in figure 4.8. on the next page.

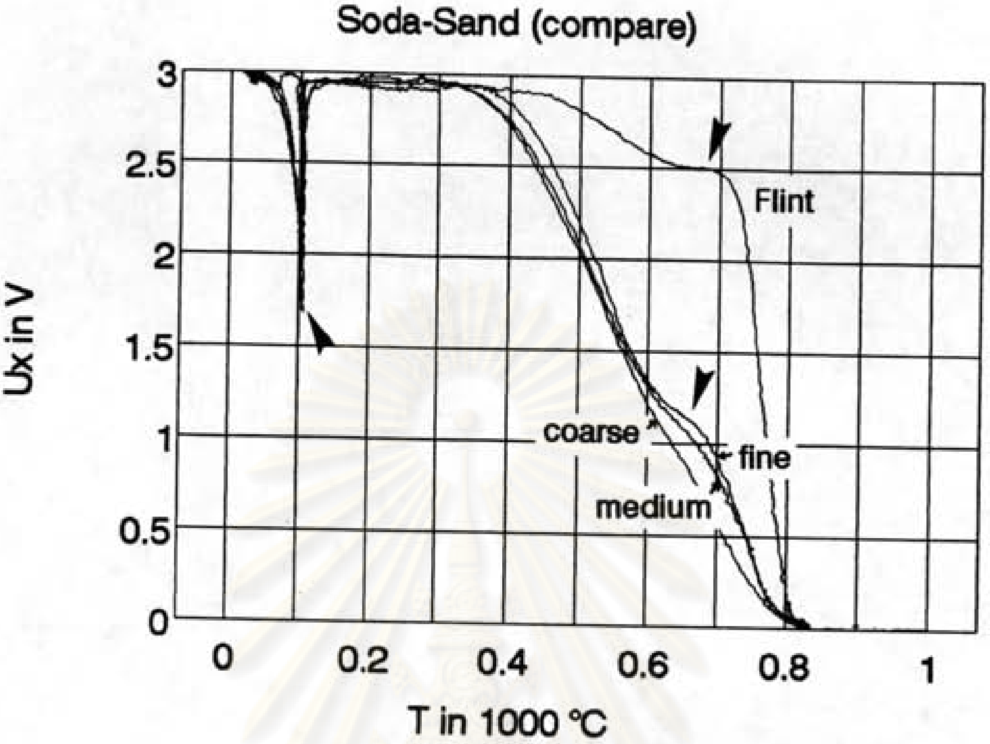


Figure 4.8 High-T behavior of Soda-Sand system

In generally, these four compositions have the same melting pattern; they all melt at 830 to 840 °C, which is attributed to the sodium metasilicate and disilicate eutectic. Also all resistivities decreased at a temperature ~ 105 °C due to dehydration of crystal water from Na_2CO_3. Differences are observed in the solid state range. Resistivities decreased again at a temperature of 380 °C for coarse and medium size of sand, of 410 °C for fine sand, and of 450 °C for flint. All four compositions had the same resistivity "nose" (change of slope) at 600-700 °C. This is attributed to the onset of a solid state reaction when the soda starts to react with sand grain to form metasilicate and disilicate;

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

$$Na_2CO_3 + 2SiO_2 \longrightarrow Na_2Si_2O_5 + CO_2$$

X-ray data by (R.F.Speyer, 1993) support this interpretation. They find maximal metasilicate at 600 °C, and disilicate at 720 °C, respectively. The decreasing rates of resistivity for the four mixtures were different. Coarse, medium and fine sand are nearly the same, but flint has a much lower decreasing rate in the beginning and higher decreasing rate at the final state (meta-silicate and disilicate formation). The big nose indicates that substantial amounts of Na^+ are immobilized in newly generated phase. This is, firstly, due to the large specific surface area of the flint (> 500 cm^2/g). In part, it may also be due to the CO_2 partial pressure in the system. For flint, it is higher than for coarse and medium size sand. (see figure 4.9) because of the small voids between the grains.

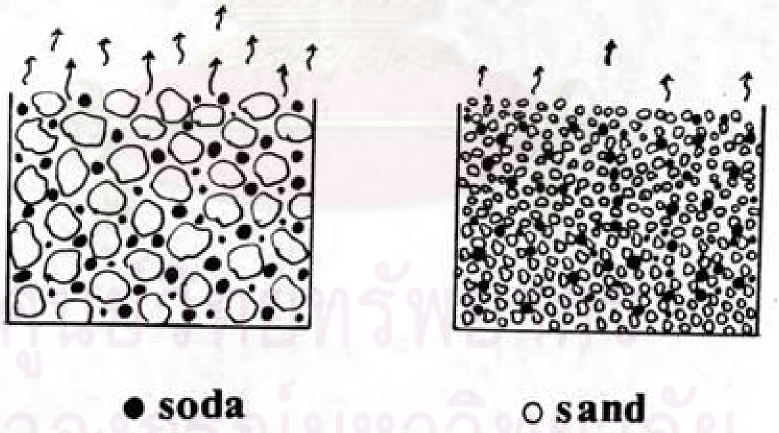


Figure 4.9. Effect of particle size on CO_2 release.

Liquid phase occurs at 830-840 °C as said above. The reaction of quartz grains is further enhanced with molten soda (>850 °C). Physical melting of soda shows a prolonged endotherm for about 20 min (see figure 4.10). For reasons of clarity, the temperature-time curves are shifted relatively to the time scale. The onset of each curve corresponds to t=0. The same procedure is also used with all the following temperature-time plots.

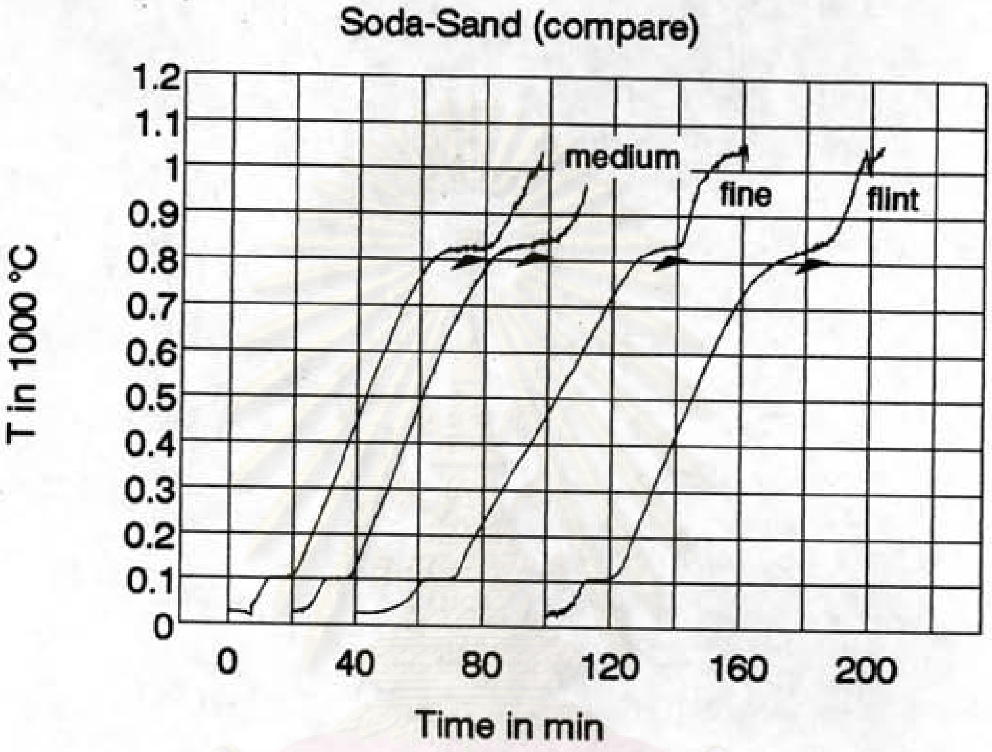
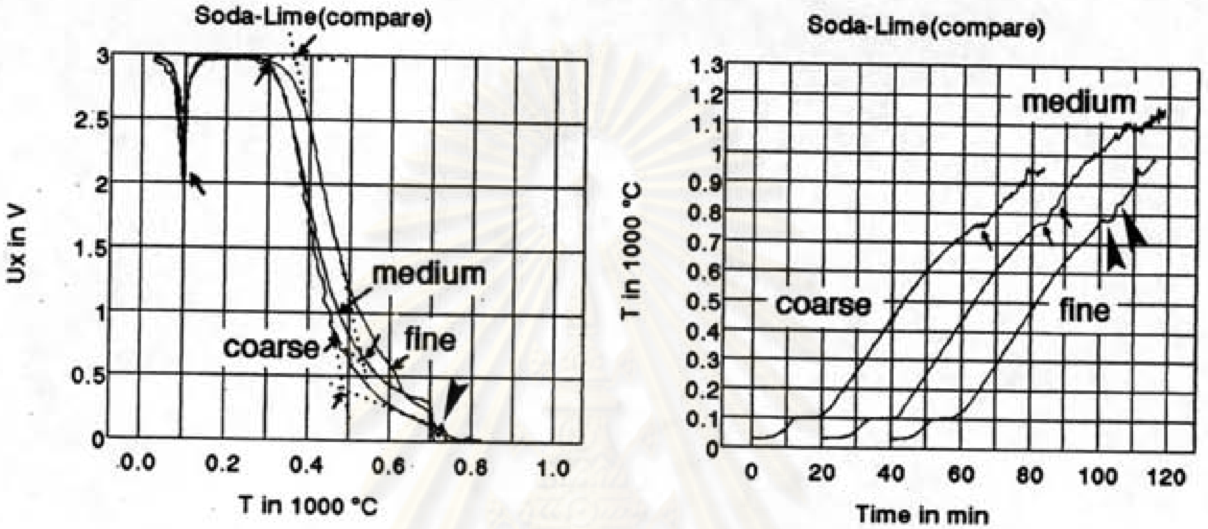


Figure 4.10 Batch temperature of Soda-Sand system.

Soda-lime system

In this system, the normal size of soda was mixed with 3 different sizes of limestone (coarse, medium and fine). The dehydration of crystal water from soda ash is found at 105 °C again as like in the soda-sand system. The cross-over temperature occurs at 320 °C for coarse, 330 °C for medium and 360 °C for fine lime (see figure 4.11). The resistivity decreases at lowest temperature for the coarse limestone. At 490-540 °C range, the slopes decrease. This was a reaction also found to have an effect by slowing down weight loss found in of DTGA experiments (Speyer, 1993). The temperature of primary melt formation of these compositions were nearly the same at 720 °C, however, smaller size of limestone tend to be lower than the others.



(a) (b)

Figure 4.11 High-T behavior of Soda-Lime system a) resistivity. b) batch temperature.

The batch temperature (see figure 4.11 b.) shows 3 points which were very interesting. Firstly, this is the dehydration of crystal water from soda ash at 105 °C. Secondly, the constant level at 785 °C. This is caused by a eutectic melt of double salt and Na_2CO_3 (see phase diagram on figure 4.12). The third point is the small endotherm level at 820 °C. This is because of the fusion of residual double salt. Finally, endotherm above 900 °C indicate the dissociation of residual limestone, immersed in carbonate melt.

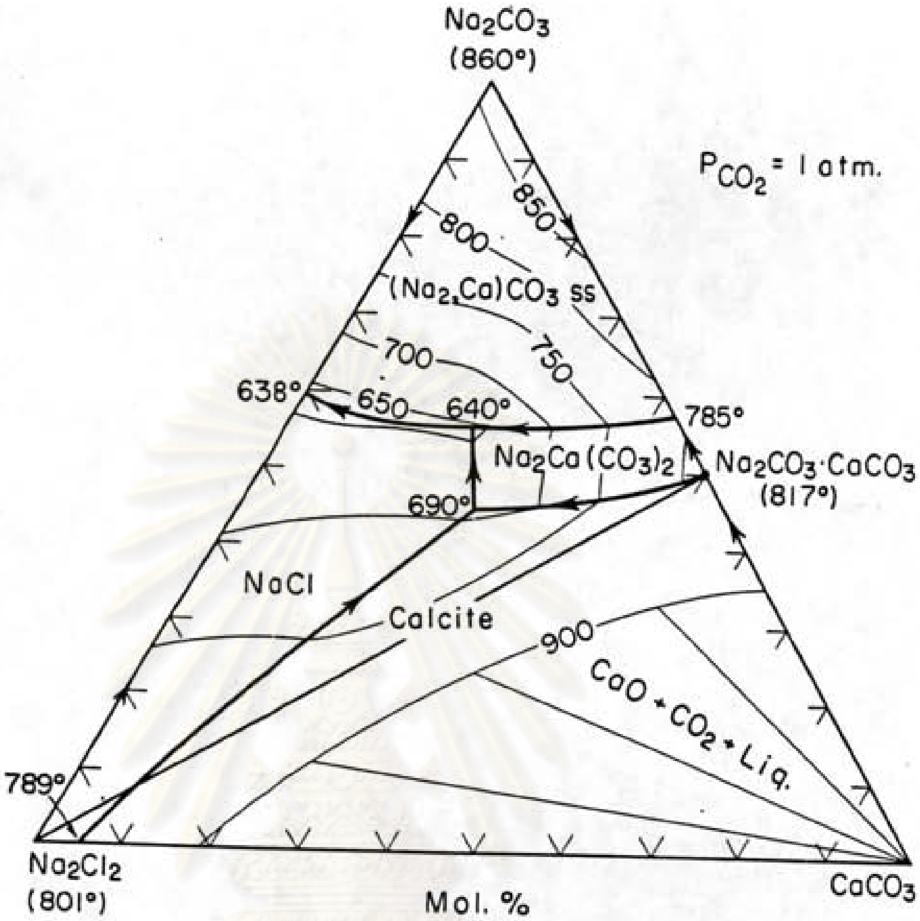
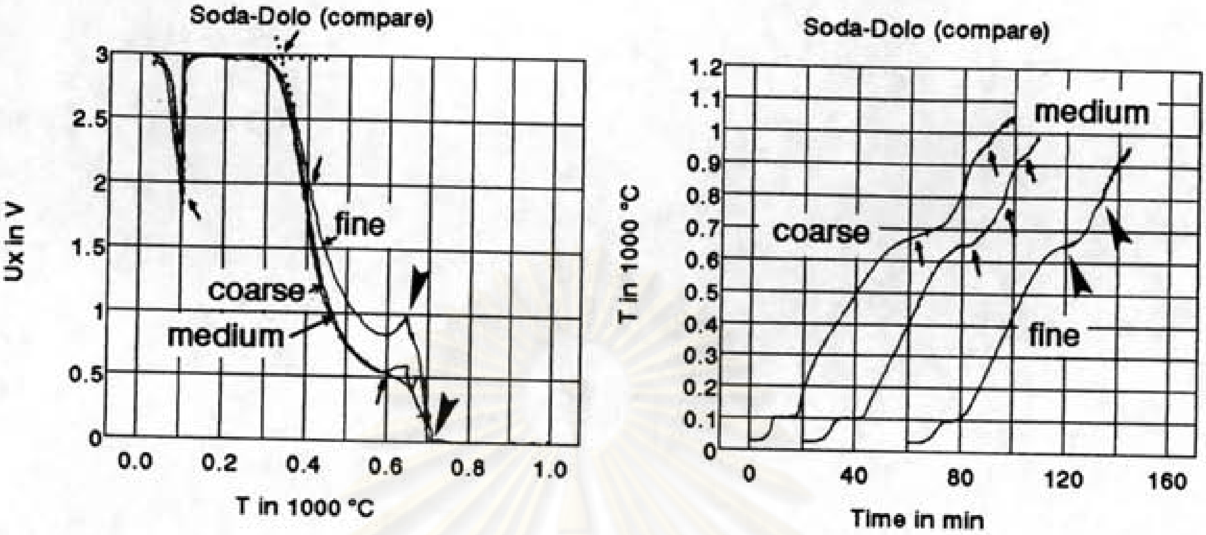


Figure 4.12 Phase diagram of NaCl-Na_2CO_3-$CaCO_3$ system

Soda-dolomite system

Three mixtures of this system were studied; industrial grade soda ash mixed with 3 different size of dolomite in the ratio of 1:1. From figure 4.7. the same resistivity peak of dehydrate water at ~105 ^{o}C were found. The cross-over temperatures were formed at ~320-330 ^{o}C (320 ^{o}C for coarse, 330 ^{o}C for medium and fine). The decreasing rate of these compositions slowed down at ~ 420-600 ^{o}C (slope changing). There is a resistivity peak at ~ 650 ^{o}C. The increase of resistivity indicates compound formation, also confirmed by the fact that a constant temperature was found at 650 ^{o}C. (see figure 4.13).



(a) (b)

Figure 4.13 Melting behavior of Soda-Dolomite system a) resistivity, b) batch temperature.

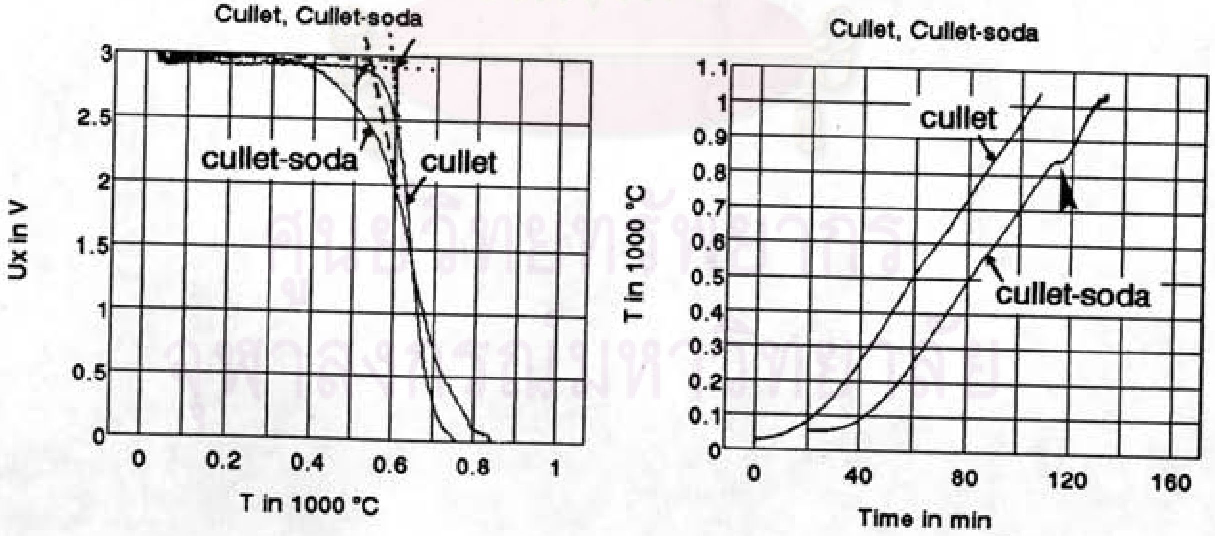
This is 70 K lower than CO_2 release from dolomite alone. Finally, at 700 °C, primary melt occurs. The finding sheds a new light on the thermal analysis by Speyer and co-workers (Speyer 1993). The authors are correct in so far as to interpret the event at 700 °C (they detect 706 °C) by eutectic melting among MgO, $CaCO_3$, and Na_2CO_3. The interpretation of the event at 650 °C in terms of liquid phase formation, however, is not supported by the present findings. This event is rather a solid state reaction yielding a yet unidentified compound.

The bench mark in batch temperature at ~ 780-813 °C indicates as eutectic melting of $CaCO_3$ and Na_2CO_3 (the same as in the soda-lime system). At ~920-950 °C, the decomposition reaction of residual limestone is clearly detected in the composition of coarse and medium dolomite only.

4.1.3 Effect of Cullet on Batch Melting

Cullet-soda system

The cullet (table ware glass from Ocean Glass Co., Ltd) was crushed to 2-5 mm size and mixed with industrial size of soda in the ratio of 9:1. The resistivity was measured both of cullet and cullet-soda mixture as shown in the figure 4.14.



(a)

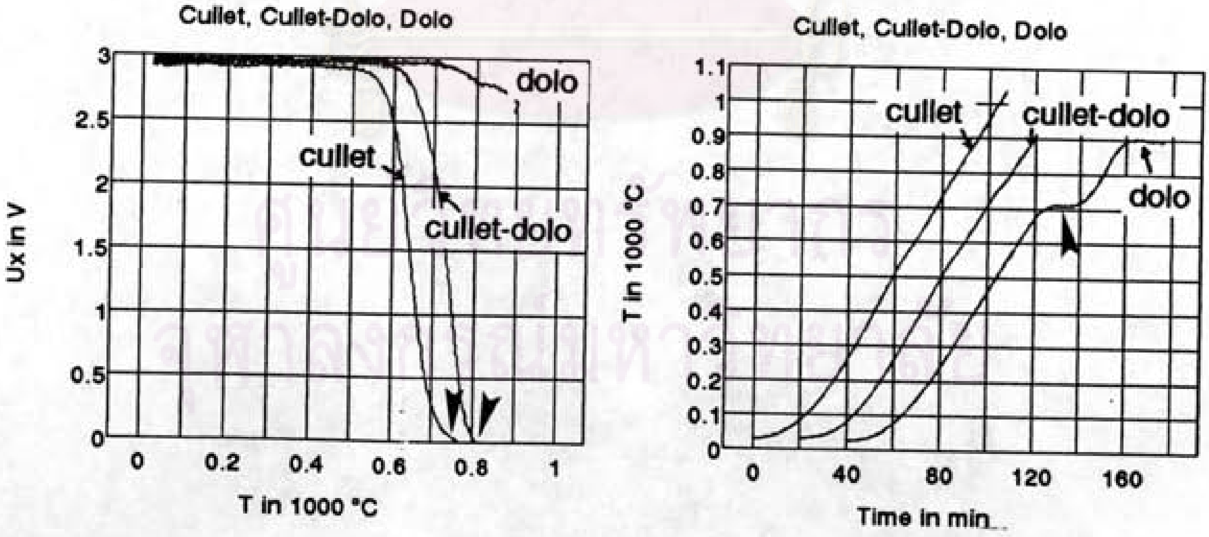
(b)

Figure 4.14 High-T behavior of cullet-soda system a) resistivity, b) batch temperature.

The result showed that cross-over temperature of cullet + soda <cullet, but the temperature of primary melt formation of cullet + soda ash was higher than for cullet alone. This is due to the fact that cullet has no melting point but melts by gradual softening (liquid phase sintering). No reactions are found as indicated by the batch temperature. In the other test, the dehydration peak of soda ash is not found, because of only 10 % soda mixed in the batch. A constant level at 850 °C in figure 4.14 indicates that the predominant reaction is physical melting of soda ash.

Cullet-dolomite system

The same cullet was used in this system. the result is shown in figure 4.15 a) and b).



(a)

(b)

Figure 4.15 Melting behavior of cullet-dolomite system a) resistivity, b) batch temperature.

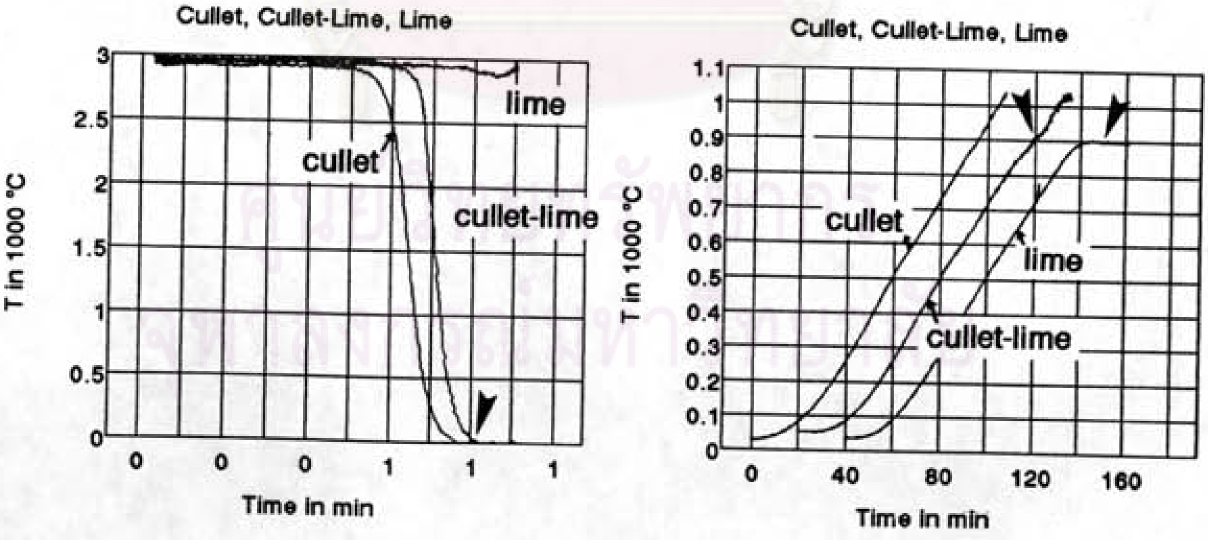
In this system, dolomite reacts as a retarder for melting reaction. The primary liquid phase occurred only 810 °C compared to 780 °C for pure cullet. The exiting observation, however, is this: dolomite chemically reacts with cullet, a fact unknown until today. The first decay step of dolomite

$$CaMg(CO_3)_2 \text{ -----> } MgO + CaCO_3 + CO_2$$

is delayed to 780 °C.

Cullet-limestone system.

The results in figure 4.16 a) and b) shows that limestone reacts with cullet in the same way as dolomite: Figure 4.16 b). shows a remarkable endotherm at 910 °C in the cullet-limestone system. This is the reaction of $CaCO_3$ ----> $CaO + CO_2$, shifted to somewhat higher temperature because the limestone is covered with cullet melt.



(a)

(b)

Figure 4.16 High-T behavior of cullet-limestone system a) resistivity, b) batch temperature.

Effect of particle size of cullet on melting behavior

The result on figure 4.17. shows that fine cullet establishes an interconnected melt faster than coarse cullet. The sizes of cullet are as followed for coarse (~5 mm), medium (~2 mm), and fine (<0.063mm).

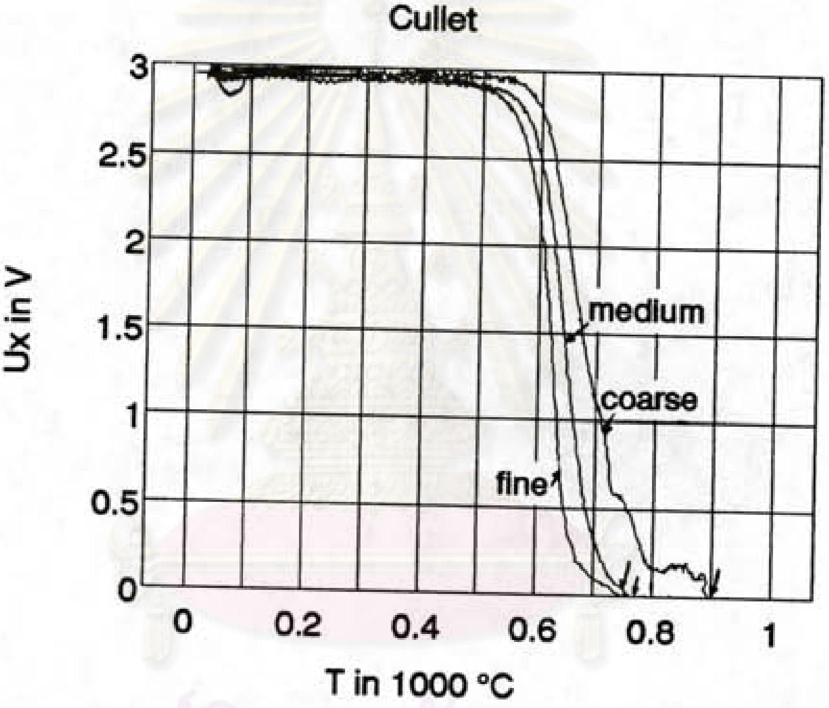


Figure 4.17 Effect of particle size of cullet on melting behavior.

4.1.4 Three Components

Eight different batches are studied. These are : 4 sets of soda-lime-sand with varied limestone particle size and 4 sets of soda-dolomite-sand system with varied dolomite particle size (as listed in table 3.6. These batches are studied at low heating rate (10 K/min).

Batches of soda-lime-sand with soda-dolo-sand systems.

In this system all batches are studied with industrial grain sizes. Limestone and dolomite batch indeed melt in different ways. Firstly, the atomic mobility in the temperature range 400 to 500 °C increase much faster the latter case. Secondly, a pronounced reaction at 650 °C (as found in the binary system soda dolomite) is seen in the latter case, while a less pronounced reaction is found at 720 °C in the former one.

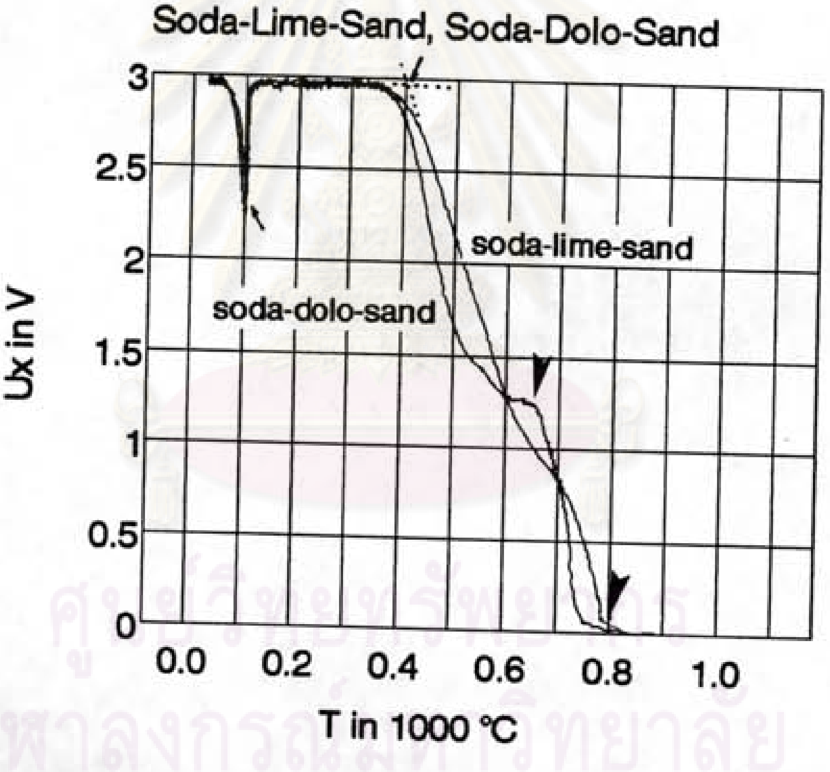


Figure 4.18 Comparison of soda-lime-sand and soda-dolomite-sand systems in industrial particle size distribution.

Size effect of limestone on soda-lime-sand system.

The reaction pattern of these systems is the same as described in the two component system. Coarse (1.000-2.000 mm), medium (0.360-0.500 mm) and fine (0.185-0.200 mm) limestone have an effect on the decreasing rate of resistivity. Coarse size tends to shows the reaction at 720 ^{o}C more clearly than the medium and fine. However, they melt at the same temperature at 785 ^{o}C, corresponding to the eutectic between double salt and soda ash. The thermal effect is shifted more and more from the eutectic temperature to the liquidus of double salt when the grains used become coarse.

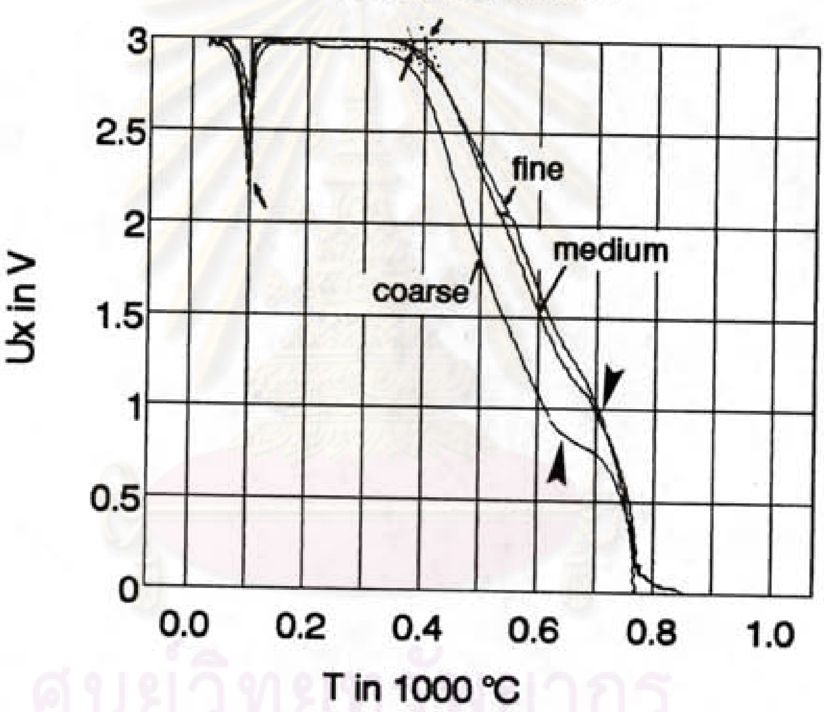
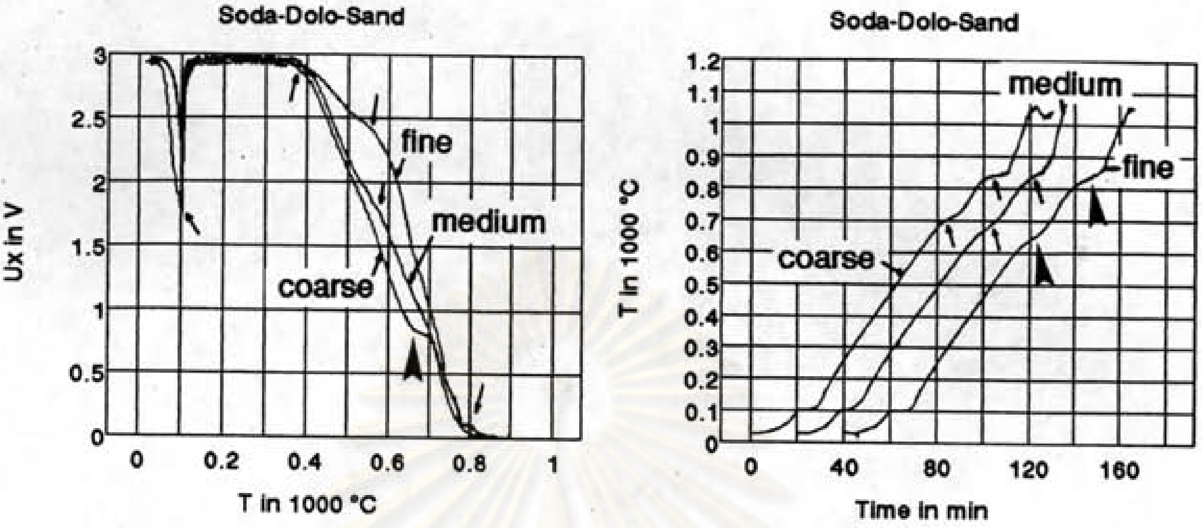


Figure 4.19 Size effect of limestone on soda-lime-sand system.

Size effect of dolomite on soda-dolomite-sand system.

The result in figure 4.20 a) and b) shows that dolomite has a strong size effect in the soda-dolomite-sand system. It refers to the solid state range. Primary liquid phase of substantial amounts is found at 840 ^{o}C (NS_2-NS eutectic) for all particle sizes. The extent of the reaction (endotherm) at 650 ^{o}C is pronounced for fine dolomite, and not seen for coarse one.



(a) (b)

Figure 4.20 Size effect of dolomite on soda-dolomite-sand system. a) resistivity, b) batch temperature.

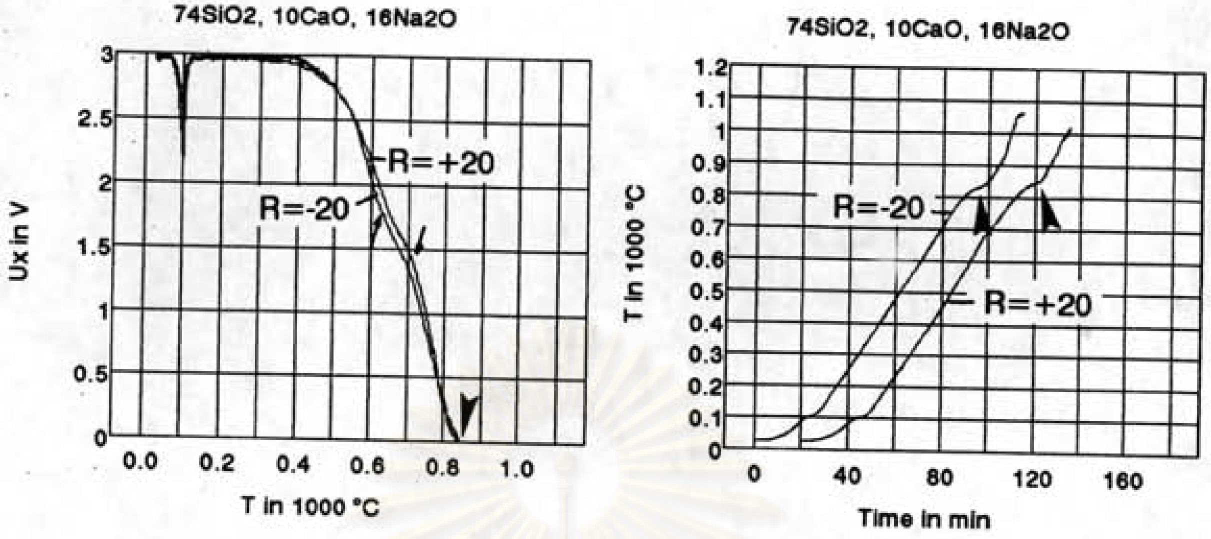
4.1.5 Multicomponent

The glass base on the composition of 74 wt. % SiO_2, 10 wt. % CaO, and 16 wt. % NaO_2 with varying redox number -20, 0, +20 was studied. Accelerants NaCl in amount of 1 wt. %, 0.3 wt.% was added 1 wt. % to the redox no -20 and to the redox number no +20 batch.

Effect of redox number on glass batch melting

The results of glass batch with R=0 is the same pattern as found in the systems of soda-lime-sand. (see section 4.1.4). Primary melt occurs at 840 ^{o}C (NS_2-NS eutectic). The same result was obtained with R=+20 and R=-20. The resistivity decreasing faster in glass batch with R=-20 than with R=+20.

The shoulder at ~630-720 ^{o}C is more pronounced in the reducing batch. Beside this, details in the reaction path cannot be seen.

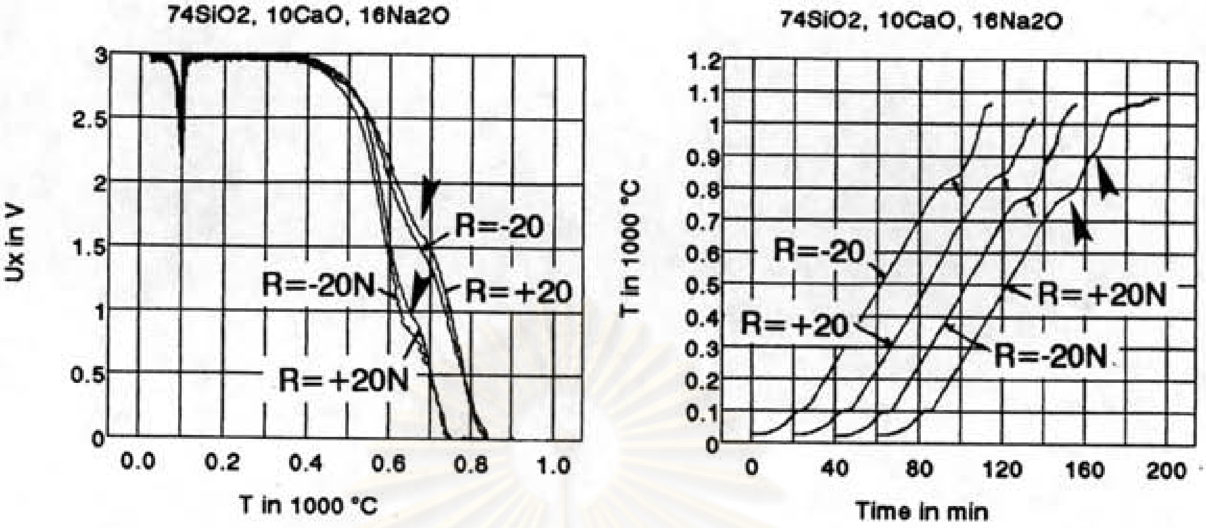


(a) (b)

Figure 4.21 Effect of redox number on glass batch melting
a) resistivity, b) batch temperature.

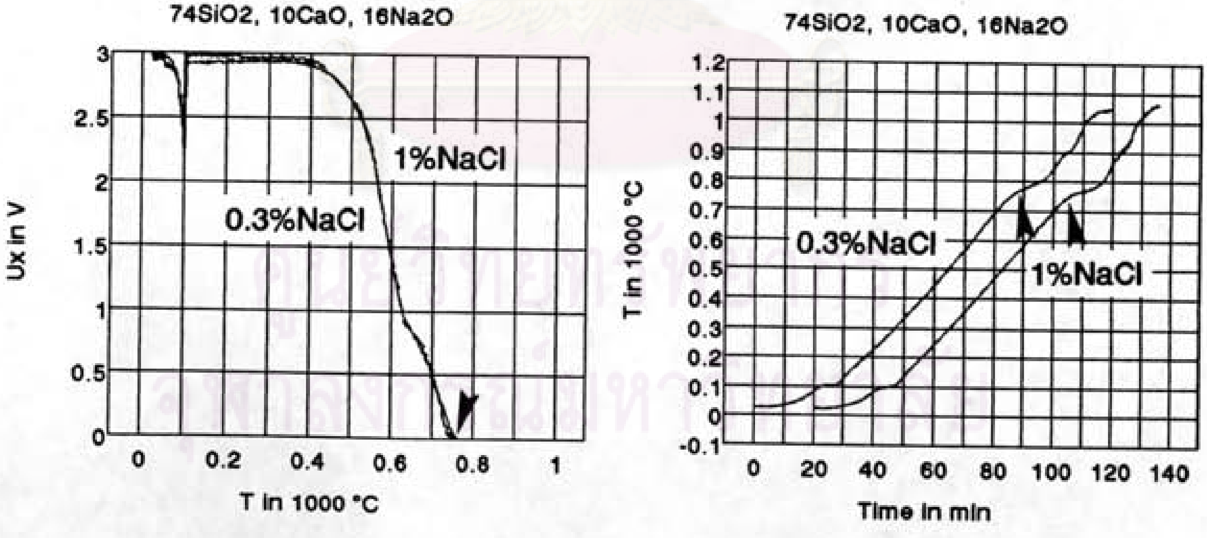
Effect of NaCl on glass batch melting

The results show that NaCl acts to accelerate the reaction of the batch. Primary melt occurs approx. 100 K earlier than in a batch free of NaCl. This is true for both oxidizing and reducing melting conditions. The temperature shows that in the presence of NaCl, the endotherm at 830 to 840 ^{o}C is no longer found. Instead, endotherms at 760 and 910 ^{o}C emerge. This indicates a fundamental change of the reaction path achieved by minor additions of NaCl. Batch containing 0.3 and 1 % NaCl give nearly the same result. This means NaCl acts as an accelerant even in small amounts. (see figure 4.23). This shows that NaCl involves in an interface-controlled reaction.



(a) (b)

Figure 4.22 Effect of NaCl on glass batch melting a) resistivity, b) batch temperature.



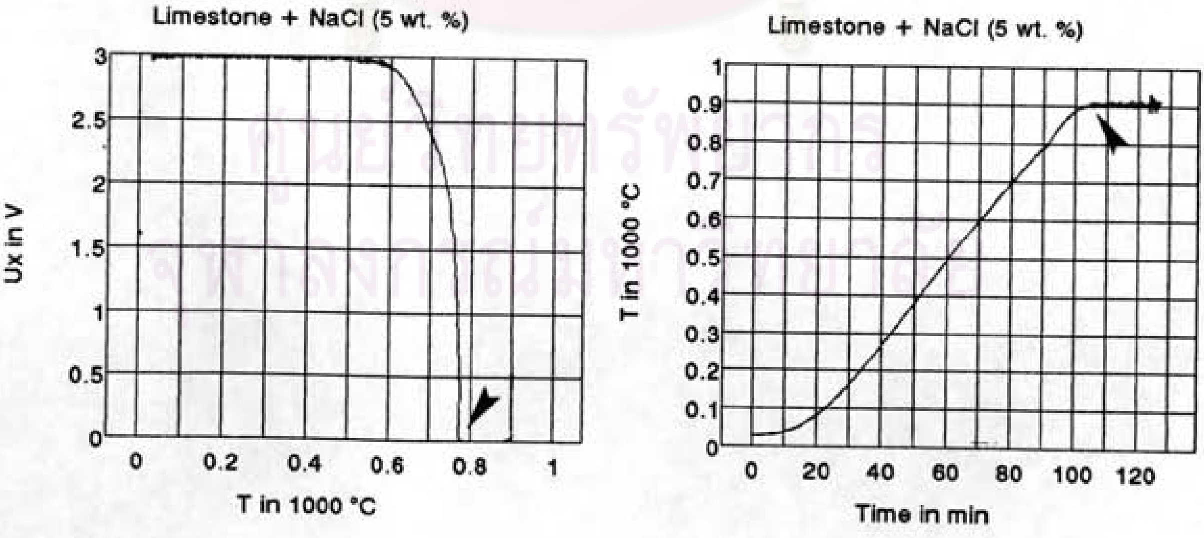
(a) (b)

Figure 4.23 Different amount of NaCl on glass batch melting. (a)resistivity, (b) batch temperature

In order to check the nature of the reaction, the following additional tests were performed:

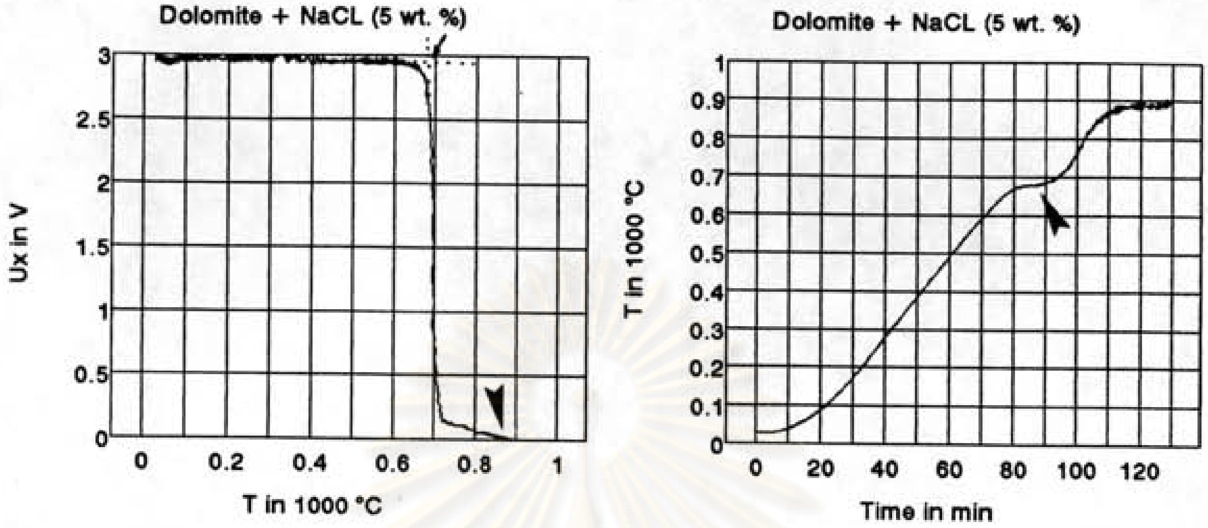
limestone + NaCl	(see figure 4.24)
dolomite + NaCl	(see figure 4.25)
sand + NaCl	(see figure 4.26)
soda + sand + NaCl	(see figure 4.27)

Both limestone and dolomite forms liquid phase with NaCl at a temperature corresponding to the NaCl-$CaCO_3$ eutectic. Sand forms liquid phase with NaCl at < 800 °C. It must be left open whether this is the physical melting of NaCl alone, or the eutectic SiO_2-$Na_2Si_2O_5$. For comparison, sand + soda forms liquid not before 840 °C (see figure 4.27). The main observation is that none of the sub-systems yield primary melt at a temperature as low as in the ternary batch. Note that thermal analysis is unable to detect anything significant at 700 °C. The present work thus confirms the three-phase mechanism proposed by Ginstling et al.(Ginstling 1952).



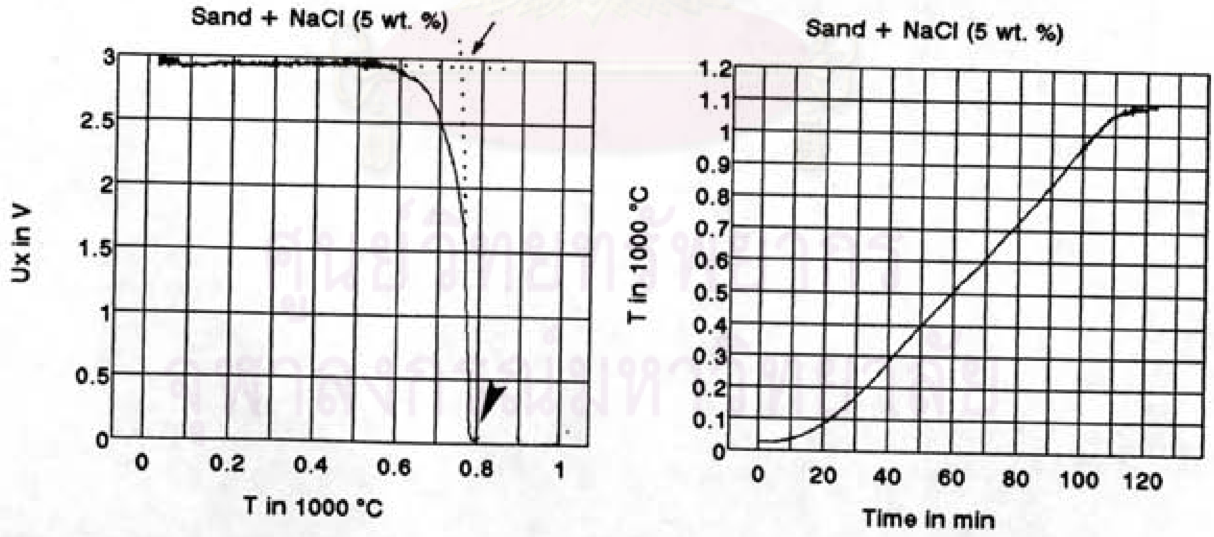
(a) (b)

Figure 4.24 High-T behavior of limestone with 5 % NaCl (a) resistivity, (b)batch temperature.



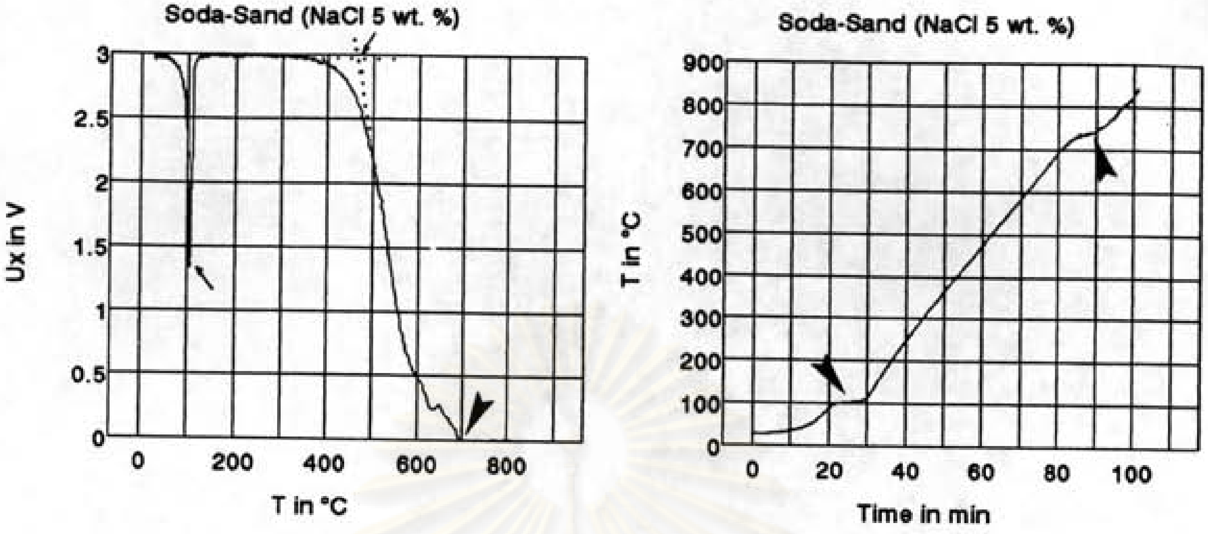
(a) (b)

Figure 4.25 High-T behavior of dolomite with 5 % NaCl (a) resistivity, b) batch temperature.



(a) (b)

Figure 4.26 High-T behavior of sand with 5 % NaCl (a) resistivity, b) batch temperature.



(a)

(b)

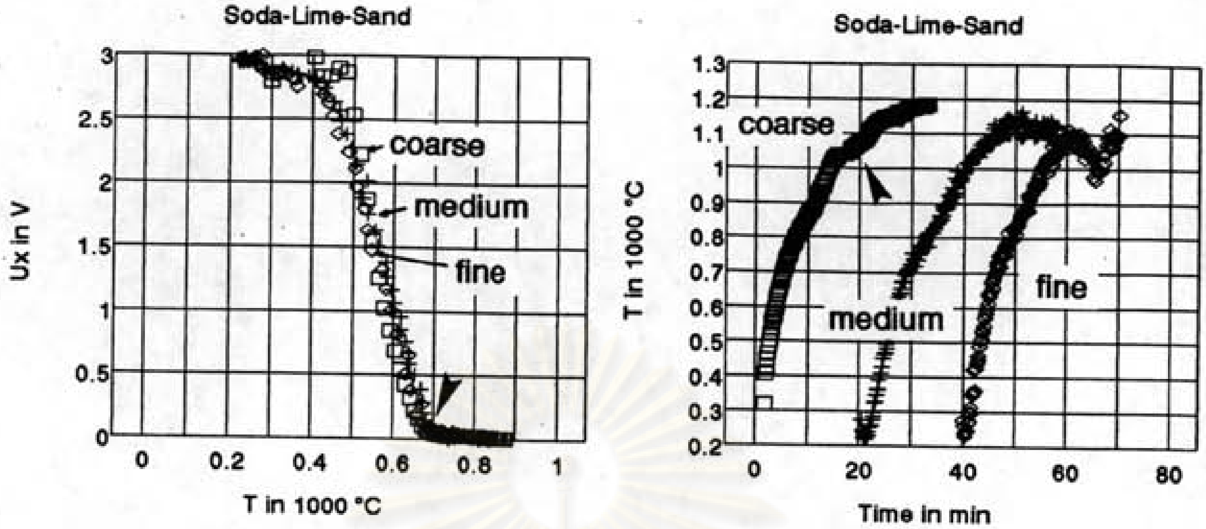
Figure 4.27 High-T behavior of soda+sand+NaCl (5 wt. %) a) resistivity, b)batch temperature

4.2 Resistivity measurement at high heating rate

The same glass batch compositions as in section 4.1.4. were studied at high heating rate. The test was done by heating up the furnace to 1200 °C. Then the batches were charged and resistivities were determined.

4.2.1 Soda-lime-sand system

The result of this system is shown in figure 4.28. The melting behavior of soda-sand-lime in fast heating rate indicated the same pattern as found in low heating rate test. But, the different size of limestone seemed to be of less effect on the melting reaction for fast heating rate.



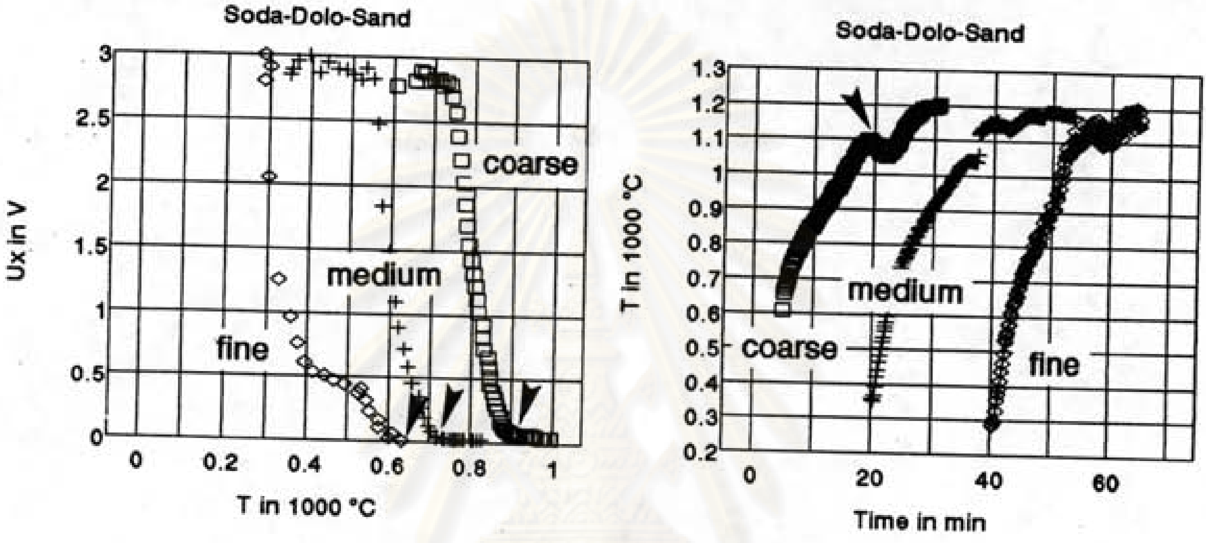
(a) (b)

Figure 4.28 High-T behavior of soda-lime-sand system a) resistivity, b) batch temperature.

This is because, upon fast heating, the soda ash particle separates from the quartz and is absorbed by the limestone grain. Upon slow heating rate, soda ash grain separates from the limestone and exclusively react with the quartz. (Riedel 1962)

4.2.2 Soda-dolomite-sand system

This system behaves totally different for high and low heating rates. The cross-over temperature started at 750 °C, 560 °C and 280 °C for coarse, medium and fine grains respectively. For low heating rate, the cross-over temperature occurred at 700 °C. Primary melt was found to occur at 890 °C, 710 °C and 640 °C for coarse, medium and fine dolomite grains. If compare with to low heating rate, this event occured at approx. 800 °C. Factory personal often report very different behavior of dolomite and limestone containing batches, which can not be understood by equilibrium data. The tests under fast heating rate, however, clearly demonstrate the dramatic difference. An explanation cannot be given yet.



(a) (b)

Figure 4.29 High -T behavior of soda-dolomite-sand system a) resistivity, b) batch temperature.

4.3 <u>DTA measurement at low heating rate</u>

4.3.1 Low heating rate test of one component system

Soda, sand, limestone and dolomite were studied. The results are shown in the figure 4.30. A number of unspecific peaks were found below 400 °C which may be due to instrumental error. They are not discussed here.

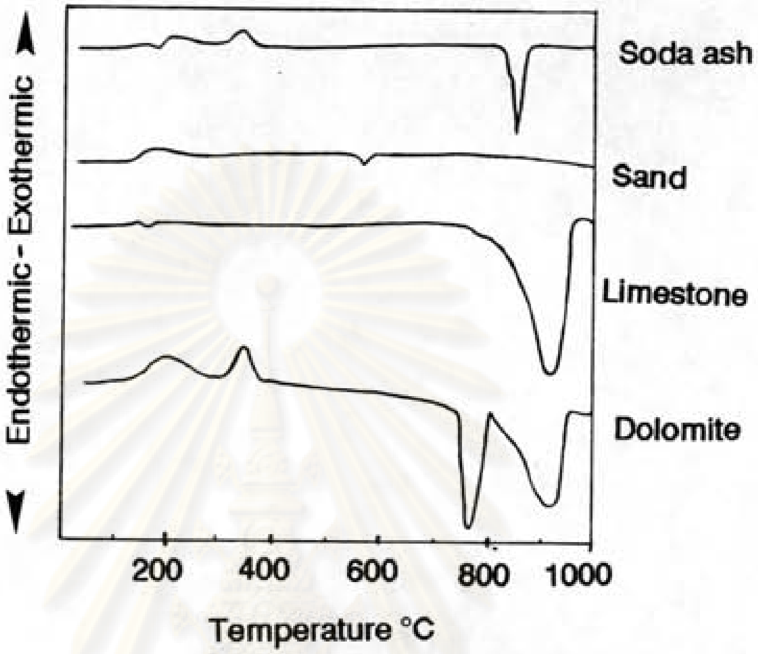


Figure 4.30 DTA traces of batch raw materials heated at 10 K/min.

According to figure 4.30, soda ash starts to melt at 819 ^oC (onset temperature of endothermic peak). $Na_2CO_3 \dashrightarrow Na_2O + CO_2$. The maximum of this peak lies at 843 ^oC.

For the measurement of sand, the quartz inversion is found at 573 ^oC and no further reaction was found.

The DTA curve shows a large endothermic peak of calcite at 907 ^oC (onset temperature at 699 ^oC). This is caused by the decomposition reaction of limestone; $CaCO_3 \dashrightarrow CaO + CO_2$. This reaction is terminated at 948 ^oC. The broadening of the endothermic peak is explained by the lack of control of the CO_2 partial pressure in the small crucible.

The endotherm of initial dolomite decay starts at 716 ^{o}C and increases until 755 ^{o}C. The endothermic peaked at 902 ^{o}C corresponds to the decomposition of free $CaCO_3$.

4.3.2 Low heating rate test of two and three components.

In this experiment, the systems of soda-sand, soda-lime and soda-dolomite were selected. The further studies were concentrated also on the system of soda-lime-sand. Figure 4.31. shows the results of these experiments.

Soda-sand system:

The result shows a small endothermic peak start at 113 ^{o}C (maximum 140 ^{o}C) due to crystal water reaction. This behavior was the same as found in resistivity measurement (the latter are being more accurate) on the system containing soda ash. The further small edothermic peak at 573 ^{o}C corresponding to the quartz inversion. The main endotherm occurs at 850 ^{o}C corresponding to the physical melting of soda ash. (see fig. 4.31.)

Soda-lime system:

Two small endothermic peaks show at 148 ^{o}C and 167 ^{o}C, the nature of which is not known. At 709 ^{o}C the melting reaction of soda-lime starts. From the literature, these mean incongruent melting of 50 mol % $CaCO_3$ and 50 mol % Na_2CO_3 at 813 ^{o}C by Niggli, 1916, and incongruent melting of 38 mol % $CaCO_3$ and 62 mol % Na_2CO_3 at 790 ^{o}C by Billhardt,1969. Both of these 2 points were found in this experiment at 807 ^{o}C and 797 ^{o}C. The small endothermic found at 879 ^{o}C, indicates the melting of "double salt" $Na_2Ca(CO_3)_2$. The shoulder line of carbonate reaction ("double salt") at 785 ^{o}C was not found (Hrma, 1982). This shows the comparative insensibility of DTA to melting reactions. The resistivity tests clearly showed the eutectic melting at 785 ^{o}C.

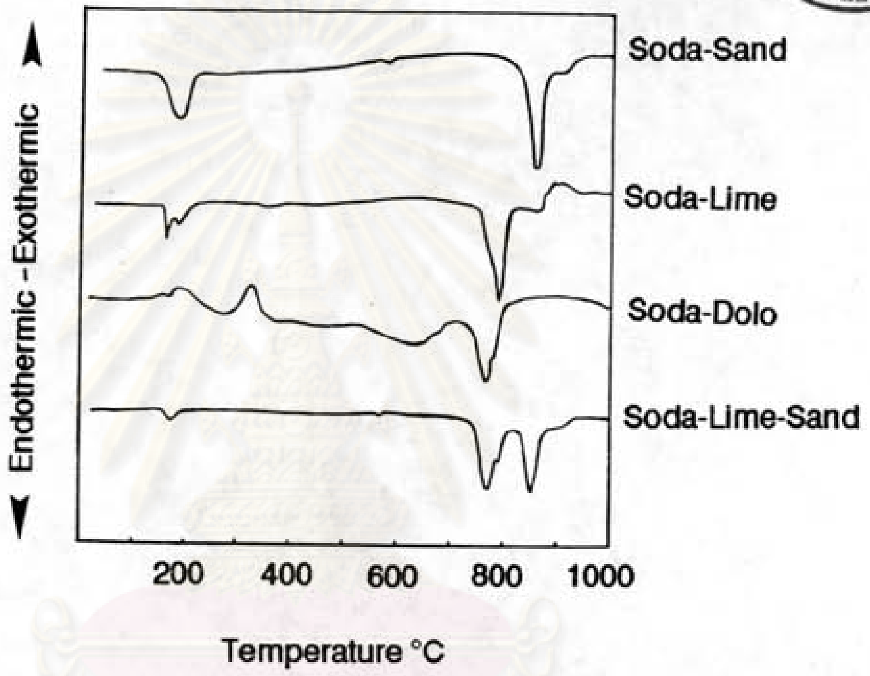


Figure 4.31 DTA traces of pairs of raw materials heated at 10 K/min.

Soda-dolomite system:

Small exothermic peaks are found at 90 ^{o}C and 251 ^{o}C. The DTA broad peak at 600 ^{o}C (maximum temperature) indicates the first step of dolomite decay to calcite and magnesium oxide. A small shoulder line at 654 ^{o}C indicates an effect from double carbonate reaction. The highest DTA peak at 744 ^{o}C and the small shoulder line at 780 ^{o}C indicate melting of double salt and Na_2CO_3. Melting of residual soda ash is not observed.

Soda-lime-sand system:

In this system, an unspecific dehydration peak was found. At 573 °C, quartz inversion of sand was found. The DTA peak at 783 °C and 801 °C indicates an incongruent melt of 38 mol % $CaCO_3$ with 62 mol % Na_3CO_2 and incongruent melt of soda and lime at 50 mol %. Temperature at 768 °C corresponds to ternary calcium sodium silicate formation. The endothermic peak at 860 °C corresponds to melting of remaining soda ash.

The DTA tests of low heating rate confirm what has been found by previous authors (e.g. Speyer 1993). New insights are not found. In comparison with the resistivity tests, strengthens and shortcomings of the DTA tests appear clearly. DTA is superior in detecting the location and extension of reactions involving heat turnover. The quartz inversion, for example, cannot be detected by resistivity. The resistivity method is clearly superior when it comes to detecting the occurrence of liquid phase.

4.4 DTA measurement at high heating rate

4.4.1 High heating rate test of one component

Soda ash, sand, limestone and dolomite were studied with the heating rate of 100 K/min. The results of these experiments are shown in the figure 4.32.

The reaction patterns are the same as in low heating rate tests, expect for a shift of the maximum peaks towards higher temperatures. Melting of soda is found at 892 °C.

The decomposition peak of limestone is broader than in the low heating rate test. The maximum peak occured at 1054 °C.

The two major reactions of dolomite are shifted to 880 °C and 1010 °C.

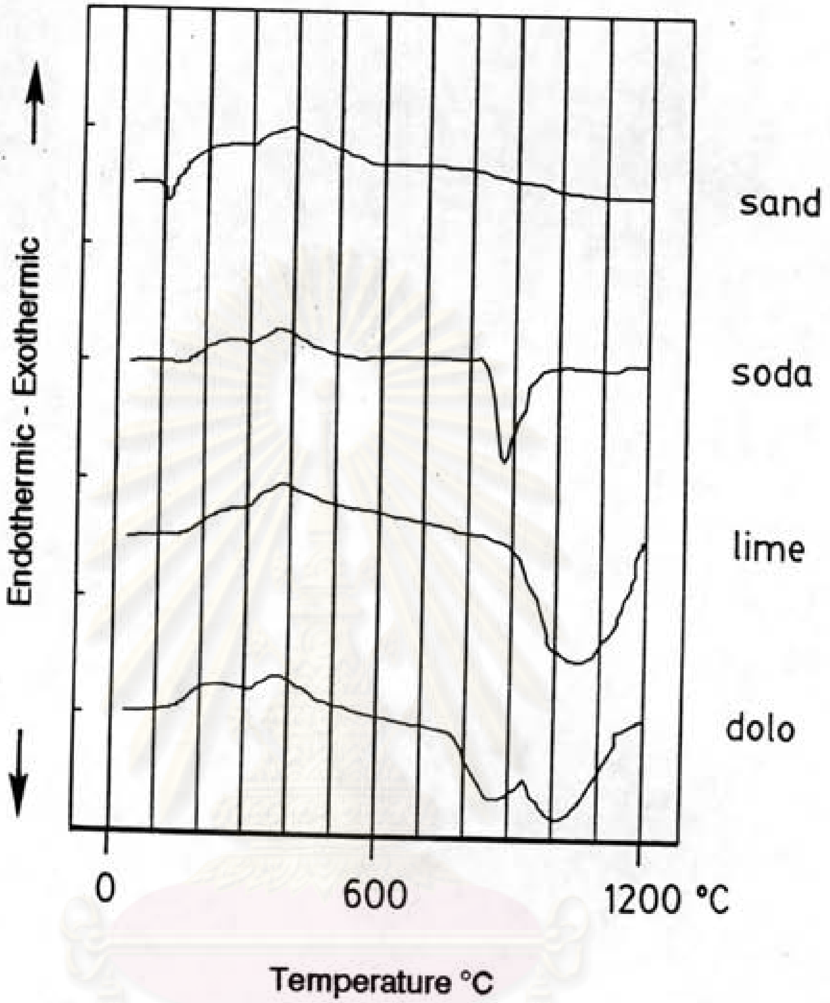


Figure 4.32 DTA traces of batch raw materials heated at 100 K/min.

4.4.2 High heating rate test of two and three component

The results are shown in figure 4.33. For soda+sand, maxima peaks occur at 890 and 995 °C. The temperatures belong to the NS-NS2 sub-system.

The DTA peak of soda-limestone is a sharp peak at 835 °C, indicating the reaction point of double salt. The most interesting part is the early onset of the reaction starting at 720 °C already. This indicates a solid state reaction

$$Na_2CO_3 + CaCO_3 \text{ ----> } Na_2Ca(CO_3)_2$$

The result of soda-dolomite system shows the same sharp peak at 835 °C. The onset shows the dolomite decay (first shoulder) and the solid state double salt formation reaction (second shoulder). The onset temperature of the decomposition reaction of dolomite starts at 685 °C. At 775 °C, the melting reaction of soda lime starts. The maximum peak of this reaction is indicated at 820 °C.

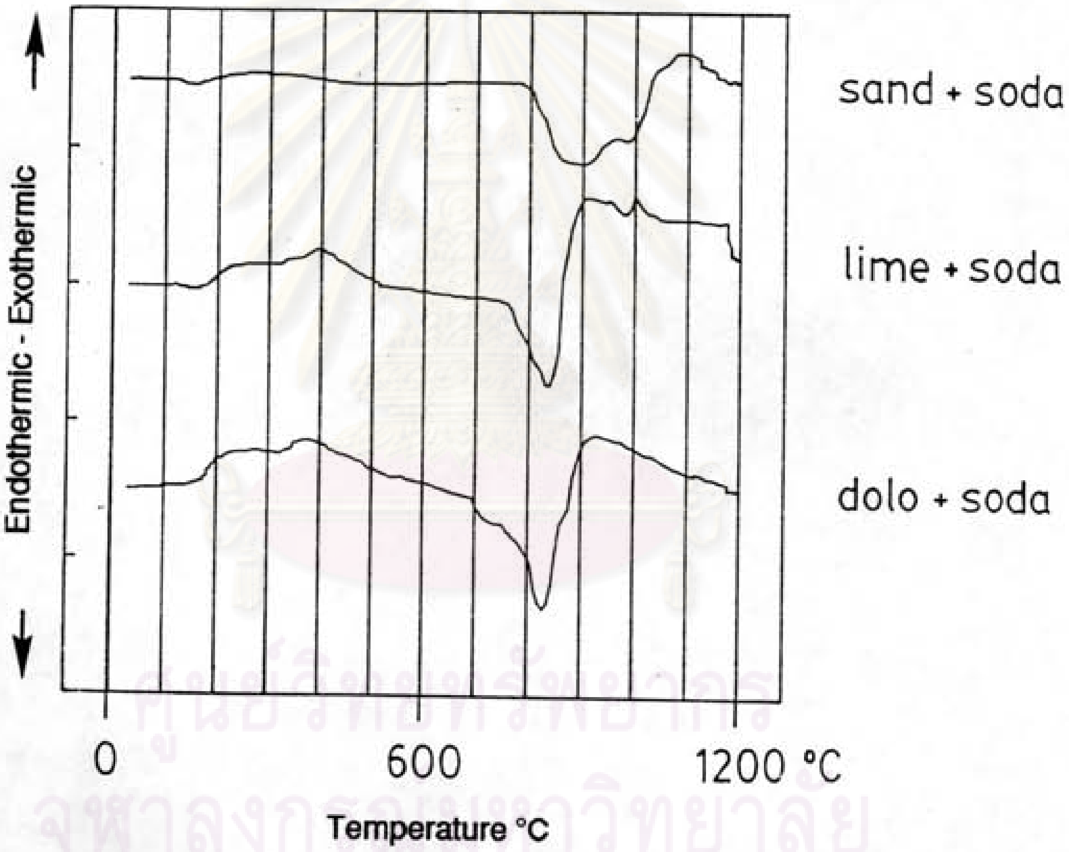


Figure 4.33 DTA traces of pairs of raw materials heated at 100 K/min.

4.5 Oxygen activity measurement

Figure 4.30. illustrates how the redox active in a batch influence the oxygen partial pressure at the interface melt/batch. The investigated batches contain (by weight) 61.5 sand, 14.8 limestone, 20.9 soda ash, 2.5 sulfate, as well as 0.15 and 0.34 coal for redox number +20 (oxidizing) and -20 (reducing), respectively. The batches are charged on top of an oxidizing cullet at 1170 °C.

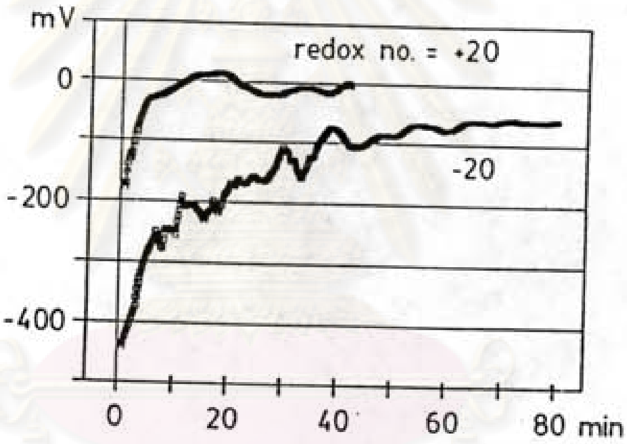
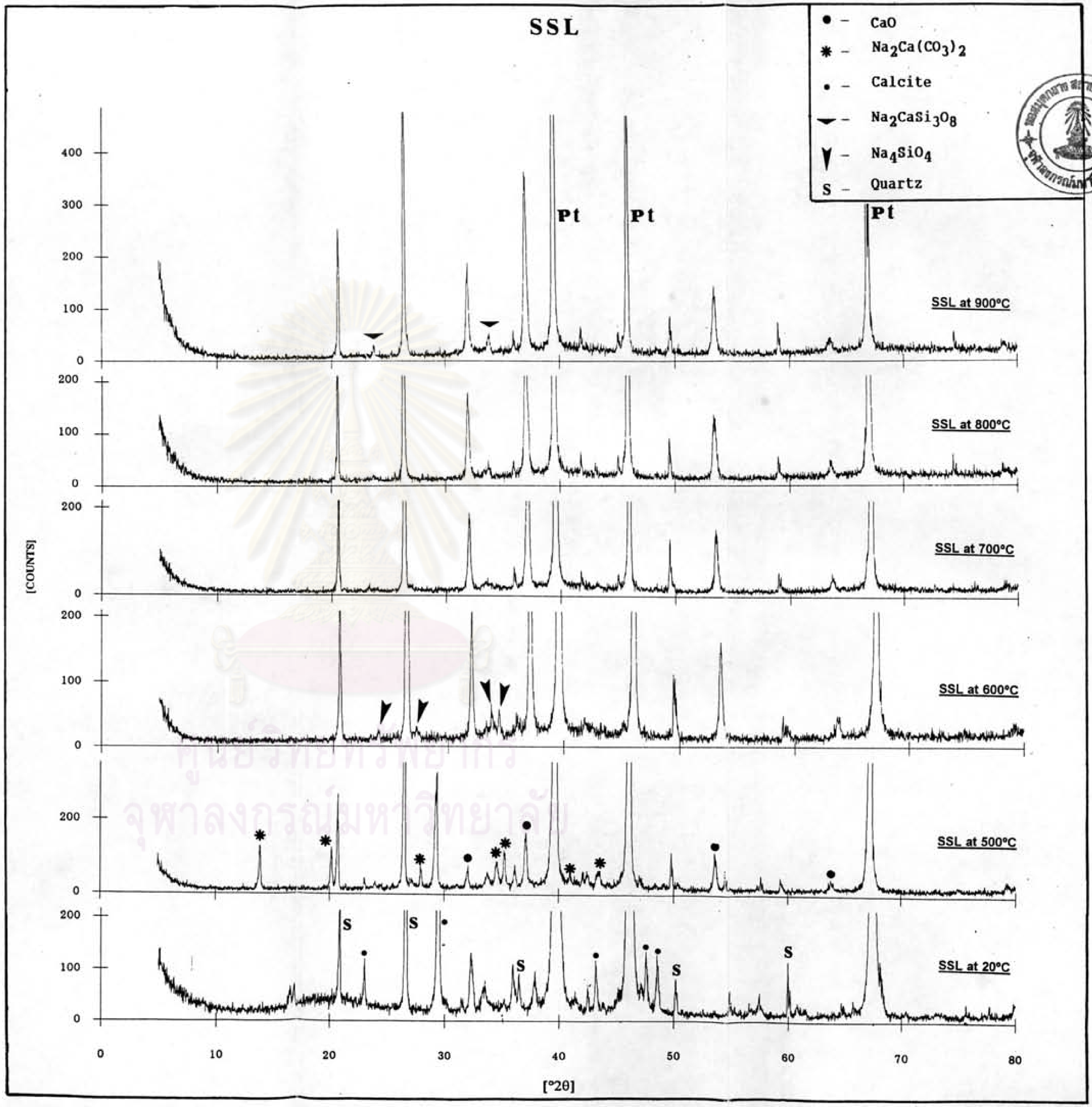


Figure 4.34 Development of the redox conditions at the interface between soda lime batches and an oxidizing cullet melt at 1170 °C; Voltage from a zirconia probe; reference gas: air

The voltage obtained from the zirconia probe is related to the oxygen partial pressure $P(O_2)$ by Nernst's equation and, in turn, to the Fe^{2+}/Fe^{3+} ratio after (M.H Chopinet, 1986), yielding

$$\log P(O_2) = -0.68 + 21.2 \cdot \text{Ø}/T$$
$$= 11.38 - 25190/T - 4 \cdot \log (Fe^{2+}/Fe^{3+}),$$

T in K, ϕ in mV. As seen from figure 4.30, coal sets free its reducing power of -450 mV for the reducing batch is close to the theoretically expected -490 mV, that is, $3 \cdot 10^{-8}$ bar O_2. As melting proceeds, the newly generated, reducing melt is absorbed by the oxidizing cullet melt, and the interface assumes mildly reducing conditions (0.03 bar O_2). It is interesting to note that, due to its carbon content, the oxidizing batch temporarily passes through a phase of reducing conditions ($3 \cdot 10^{-4}$ bar O_2) before oxidizing conditions (0.15 to 0.3 bar O_2) are reached. This shows that sulfate develops its oxidizing power at comparatively late stages of batch melting. The industrial practice to combine sulfate with saltpeter may be considered as a compensation of this behavior.



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4.6 Hot stage X-ray diffraction measurement

4.6.1 Soda-lime-sand system

A mixture of soda-lime-sand in the ratio of 1:1:1 was tested at temperatures 500 °C, 600 °C, 700 °C, 800 °C and 900 °C. The results are shown in the figure 4.35. Unfortunately, the experiments had to be performed under vacuum. The influence on most reactions is minor. However, calcite is known to completely decay below 650 °C (instead of 900 °C). The early presence of free lime CaO in the batch may initiate other reactions. So the results have to be interpreted carefully.

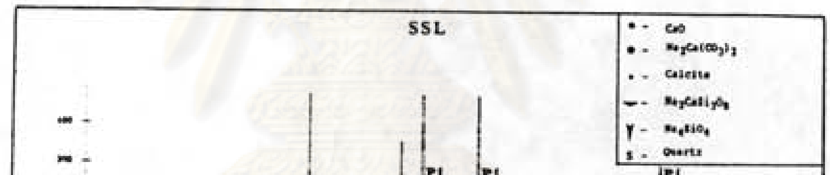
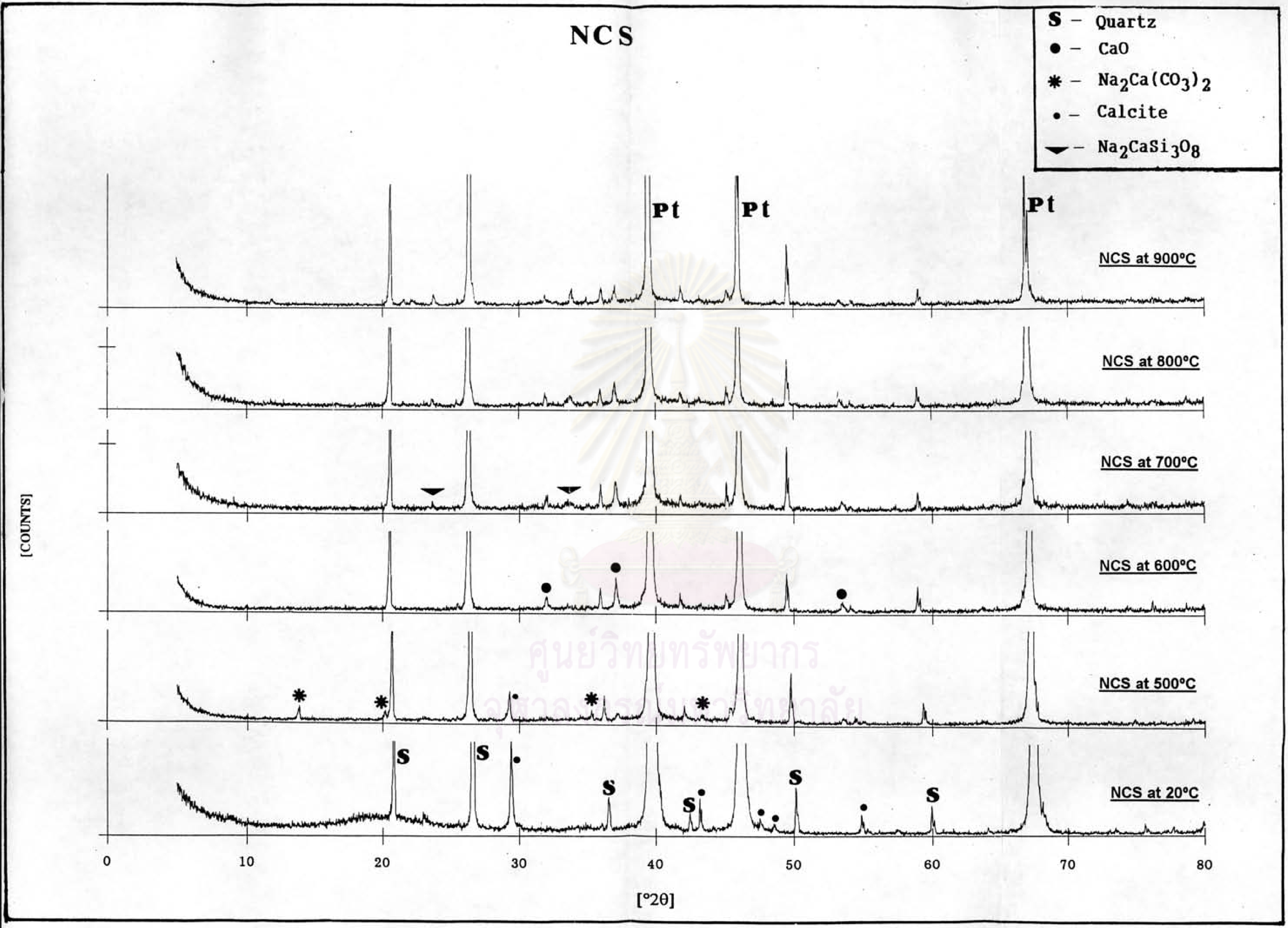


Fig. 4.35 Hot-stage XRD peaks of soda-lime-sand in the ratio of 1:1:1 system

At room temperature (assume ~30 ^oC), the test clearly shows fours phases; calcite ($CaCO_3$), quartz (SiO_2), Na_2CO_3 and $Na_2CO_3.H_2O$. The intensity of Na_2CO_3 and $Na_2CO_3.H_2O$ is not high. This may come form a not-well-crystallized soda ash raw material (precipitated material). When the sample was tested by hot-stage XRD, the interference peak from the Pt-plate occured at angles of 40^o, 46^o and 67^o. These peaks must be disregarded. At the temperature 500 ^oC, $Na_2Ca(CO_3)_2$ was detected; it disappeared at 600 ^oC. At this state, the calcite phase decreases and a small peak of CaO is found. A sodium silicate phase was detected as Na_4SiO_4 at a temperature of 600 ^oC and calcite phase disappears while the CaO intensity increases. At 700 ^oC and 800 ^oC, three phases are clearly detected. These are quartz and CaO; besides this, small peaks of $Na_2CaSi_3O_8$ (N_2CS_3) can be detected and gets more intense at 900 ^oC.

4.6.2 Glass batch composition at R = -20

The glass batch composition of 74 wt. % SiO_2, 10 wt. % CaO and 16 wt. % Na_2O with redox number -20 balanced by salt cake and coal was studied. The results are similar to those in 4.6.1, yet the calcite phase decreases and CaO increases at 500-600 ^oC already. The small peak of $Na_2Ca(CO_3)_2$ disappears at 600 ^oC. At 700 ^oC, a small peak of $Na_2CaSi_3O_8$ (N_2CS_3) starts to occur and increases with temperature. Its intensity is opposite to the CaO intensity. The results of this measurement are shown in figure 4.36.



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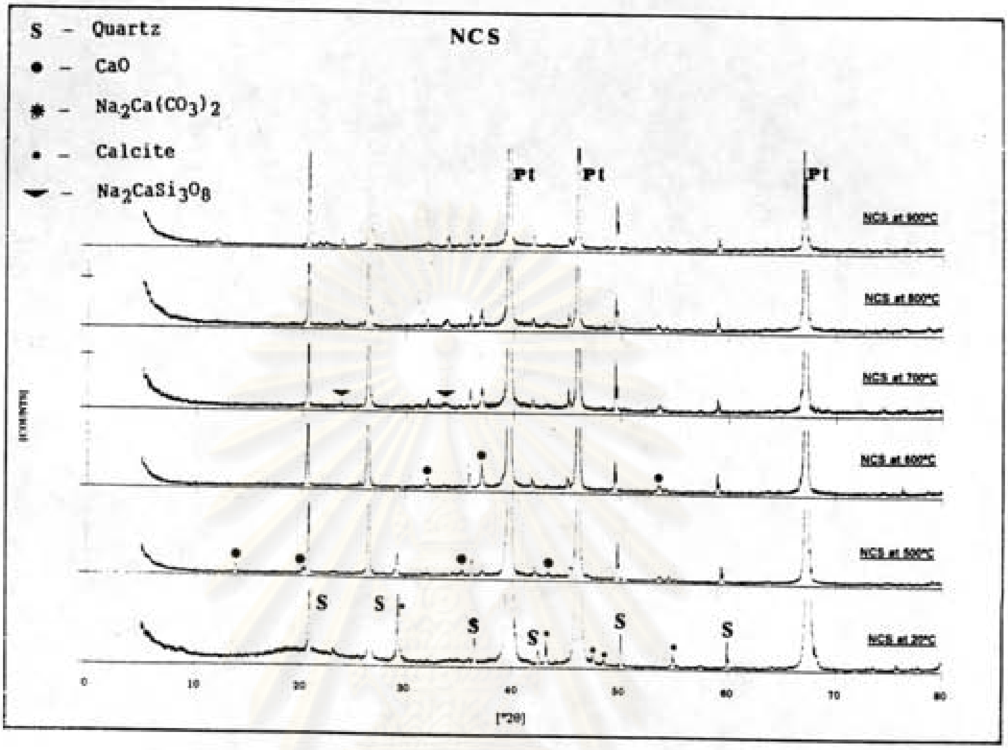
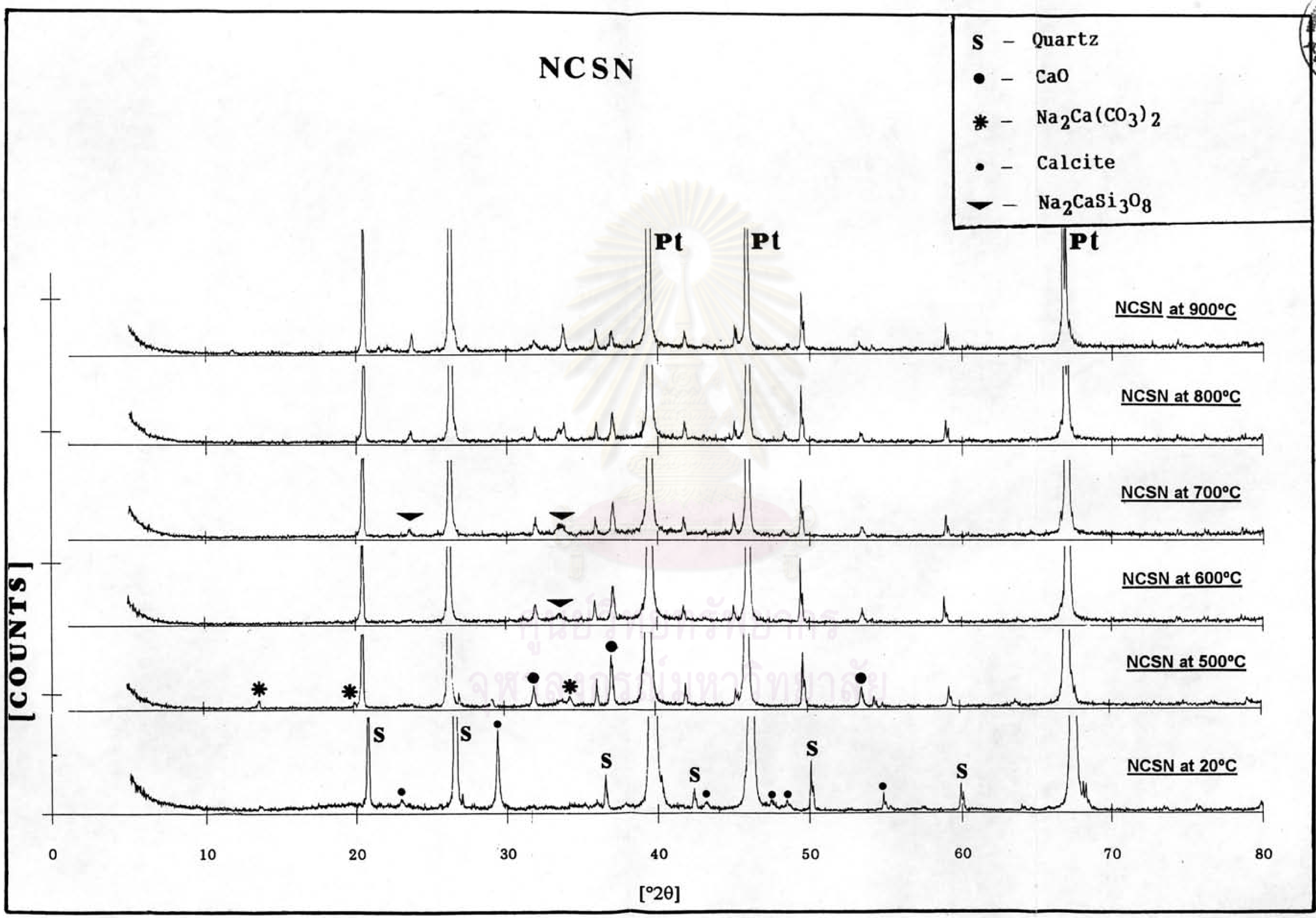


Figure 4.36 Hot-stage XRD of glass bath at R = -20

4.6.3 Glass batch composition at R = -20 with 1 wt. % NaCl

The experimental results show that nearly all calcite decomposes to CaO at 500 ^{o}C if compared with glass batch without NaCl. $Na_2Ca(CO_3)_2$ still occures at 500 ^{o}C and disappears at 600 ^{o}C. $Na_2CaSi_3O_8$ starts to occur at 600 ^{o}C already and increases with temperature; the intensity is higher than in the other tests. The results of this composition are shown in figure 4.37.



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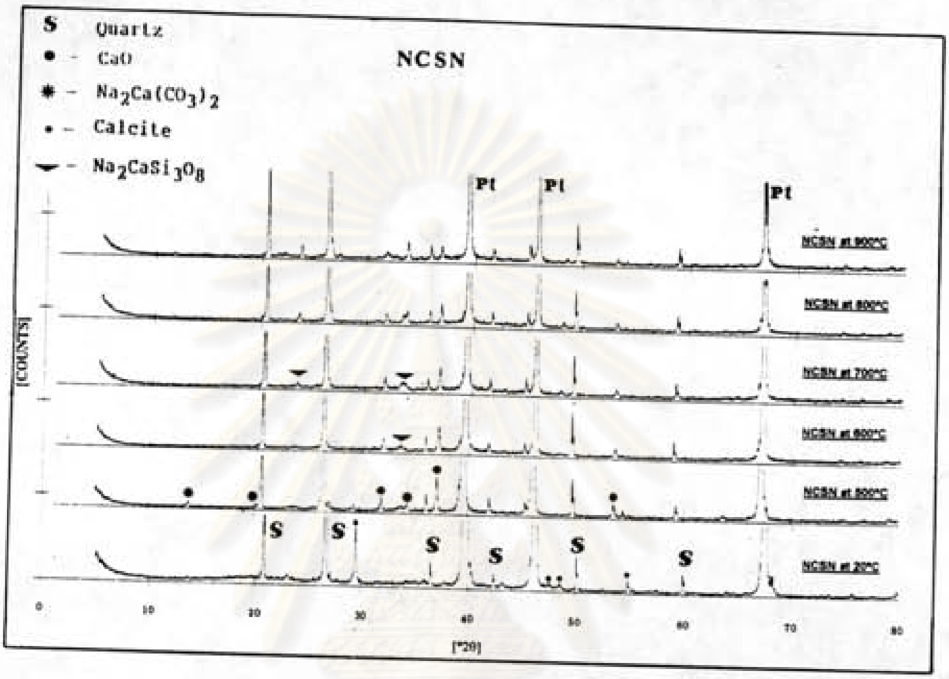

Figure 4.37 Hot-stage XRD of glass batch at R = -20 with 1 wt. % NaCl

The hot-stage XRD investigation adds a few interesting observations to complete the understanding of batch melting:

- as an experimental artifact, reactive decay of limestone occurs much earlier (from 500 °C); this must disregarded;
- the presence of NaCl enhances limestone decay;
- double salt is formed in remarkable amounts by a solid state reaction;

- the key ternary silicate precipitating from the primary melt is N_2CS_3, which is an incongruently melting compound located at the joint NS-CS (see appendix B)
- presence of NaCl strongly enhances the formation of N_2CS_3;
- the main solid phases entering the stage of "rough melt" are quartz and CaO.

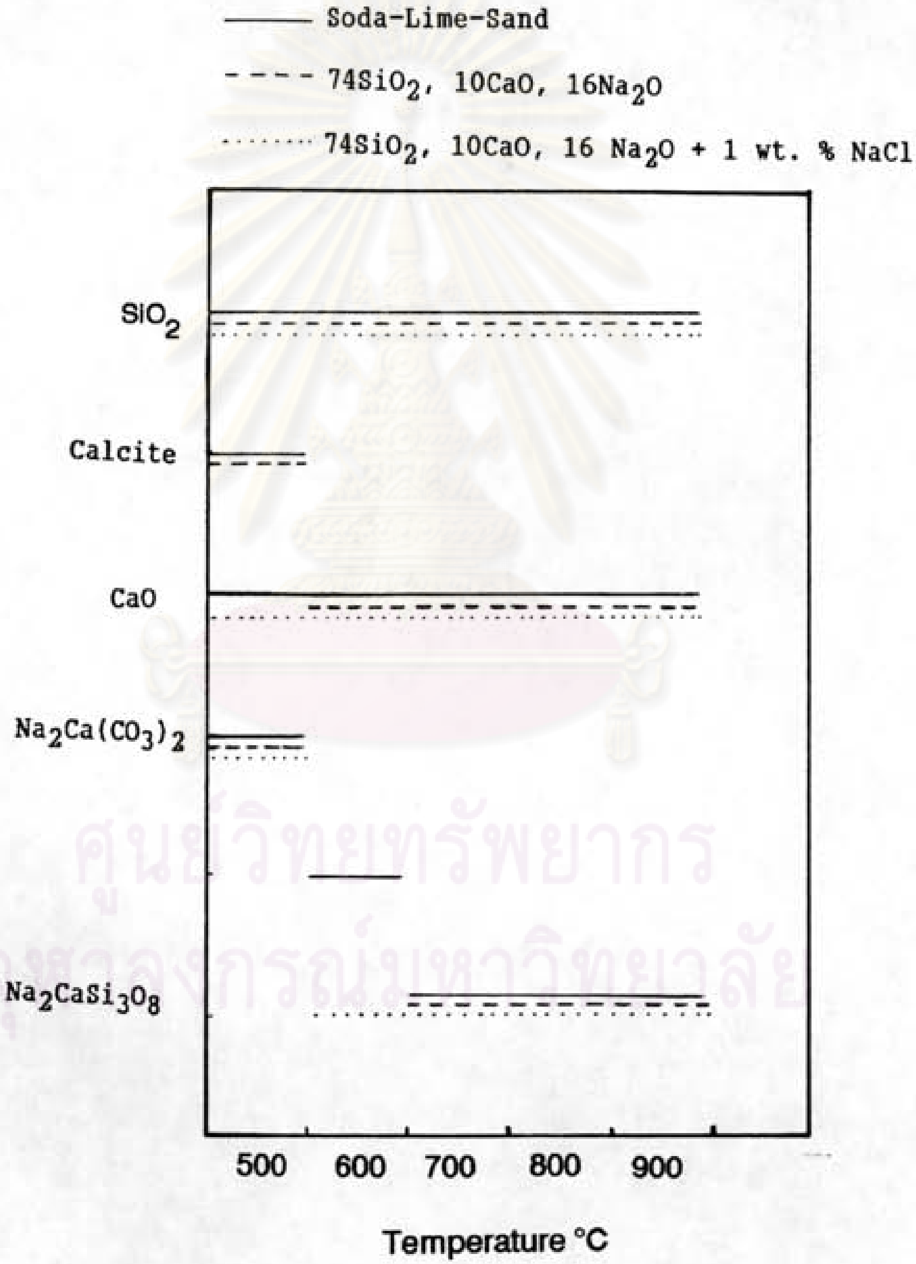

Figure 4.38 Comparison of the phases which are identified for three series of batches by hot-stage XRD