

Selective Batching for Improved Commercial Glass Melting

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Executive Summary

The overall goal of the project was to determine if alternative batching methods used in the commercial glass industry would result in improved melting behavior. Improved melting would enable shorter residence times in the glass tank, translating into direct reductions in energy intensity. We proposed that initial reactions between alkali and alkaline earth salts in the batch create a low viscosity melt that segregates from quartz particles, resulting in a mixture that must then be re-homogenized in the tank. The thesis of this project was that segregation can be limited by narrowing the range of melting points of the batch constituents and by increasing the viscosity of the molten phase formed during heating. To control the melting sequence and consequently the viscosity of the molten phase(s), we proposed to selectively batch raw materials into mixtures that form higher viscosity “endpoints,” instead of simply mixing all of the batch components together prior to charging. Specifically, the idea is to eliminate high-temperature segregation within the batching process, rather than allow the melting process to dictate the composition of the segregated species.

The general approach taken to control segregation was to separate the reactions between quartz and soda ash and quartz and limestone/dolomite. This was tested using two methods: I) selectively batch and pelletize to form small “reaction volumes” that react initially to form an intermediate reaction product; or II) pre-react selective batch components to form an intermediate feedstock. Feedstocks for Approach I were produced by spray drying two binary mixtures of quartz + soda ash and quartz + limestone/dolomite. For Approach II, the same mixtures were heated to 1400°C and quenched. Feedstocks for both approaches were then mixed and heated in crucibles until a batch-free melt was produced. The current mixed batch formulation from Guardian Glass was used as a control.

Although melt segregation was not directly observed, the results of the melting experiments indicate dramatic reductions in the time for both approaches relative to the standard batching method. The spray dried materials (Approach I) of $\{\text{Na}_2\text{CO}_3+\text{SiO}_2\}$ and $\{\text{CaCO}_3+\text{MgCO}_3\cdot\text{CaCO}_3+\text{SiO}_2\}$ were batch-free in 45 minutes at 1350°C and the pre-reacted materials (Approach II) of the same components were batch-free within 20 minutes at 1350°. A standard commercial batch (supplied by Guardian Glass) exhibited a batch-free time on the order of 240 minutes for coarse (350mm) and 120 minutes for fine (45mm) quartz, demonstrating that the benefits are not simply an artifact of particle size. Compared to the current practice, Approach I reduced batch-free time by a factor of 5.3 (an 81% reduction) and Approach II yielded a reduction in batch-free time a factor of 12 (a 92% reduction).

While the pre-reacted mixtures have a shorter batch-free time, the energy needed to pre-react then to heat the materials again in the furnace makes this method unsuitable for commercial melting. However, the spray dried route offers significantly shorter residence times in the glass tank (translating to direct reductions in energy use and emissions of criteria air pollutants) with modest increases in batch preparation costs. Overall, conservative energy savings using the selective batching approach compared to current methods are on the order of 20-33% for the entire process, assuming that melting times can be reduced by 50%. We estimate that a 700

ton/day flat glass plant that implements a selectively spray dried bathing process will reduce energy needs by 664 billion Btu, or approximately \$3.3 million. Further investigations and intermediate-scale melting trials are needed to further investigate the effect of particle size, the potential to reduce fining times, and to determine the economic feasibility of spray drying.

Project Description

1. Original project goals and objectives

The proposed goals of this project were to 1) demonstrate that large-scale segregation occurs within the glass batch during the initial stages of melting; 2) evaluate selective batching via partial batch pelletizing (Approach I) as a means of reducing large scale segregation; 3) evaluate pre-reacting (Approach II) and pre-melting (Approach III) batch components to form an intermediate feedstock; and 4) generate discussions with industrial participants to determine the feasibility of implementation on an industrial scale.

2. Variance from original goals and objectives

The overall goals and objectives were pursued as proposed in the original proposal. The pre-melting approach (III) was not pursued as it was deemed too energy intensive.

3. Discussion of work performed

The tasks performed and results are discussed under the specific tasks described in the proposal.

Task A. Binary reactions:

Several binary components (pairs of Na_2CO_3 , Na_2SO_4 , CaCO_3 , MgCO_3 , and quartz) will be batched, melted to form a homogeneous melt, then re-melted in a high temperature viscometer to determine the dependence of viscosity on temperature. The reaction rates, melting, and decomposition temperatures will be determined by simultaneous DTA-TGA and verified by literature values where possible.

Reactions for all binary pairs were measured, with the exception of Na_2SO_4 . The amount of Na_2SO_4 typically added for a commercial float glass composition was deemed too small to affect the experiments. Experiments were not conducted using the high-temperature viscometer because it was not available and the data were not critical to the success of the project, as described below.

Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (SDT 2960, TA Instrument, New Castle, DE) were performed on binary mixtures of Na_2CO_3 and CaCO_3 in a 1:1 molar ratio and each individual raw material. Temperature was increased up to 1000°C at a 10°C/minute heating rate. A platinum crucible was used with an alumina reference. Figure 1 shows the behavior of the binary mixture. The endothermic peak at 85.5°C indicates the dehydration of the mixture as physical water is removed. Endothermic peaks at 725.6°C and 871.3°C correspond to the formation of the eutectic liquid and increasing the amount of liquid phase with the loss of CO_2 , respectively. The weight loss between 600°C and 800°C is associated with the decomposition of CaCO_3 and above 800°C the weight loss corresponds to the decomposition of molten Na_2CO_3 . The endothermic peak at 868.9°C indicates melting of Na_2CO_3 . When DTA and TGA data are compared, it is evident that Na_2CO_3 melts first and then

decomposes at higher temperatures. DTA-TGA curves of CaCO_3 show an endothermic peak at 758.3°C , indicating the dissociation of CaCO_3 . The melting temperature for CaCO_3 and CaO is above 1000°C . DTA-TGA curves for individual materials are detailed in monthly reports 2 and 3.

The $\text{Na}_2\text{O-SiO}_2$ eutectic composition can be formed by melting a mixture of soda ash and 325 mesh quartz in 74:26 mole ratio at temperatures as low as 1000°C for less than 30 minutes. Figure 2 shows the DTA-TGA curves for this mixture, Preliminary experiments to form wollastonite from a binary blend of CaCO_3 and SiO_2 (325-mesh quartz) were of limited success so the binary blend composition was modified to generate a mixture of wollastonite and SiO_2 that corresponded to a composition in the CaO-SiO_2 binary at the point where a line drawn from $\text{Na}_2\text{O-SiO}_2$ eutectic through the typical float glass composition on $\text{Na}_2\text{O-CaO-SiO}_2$ phase diagram. The CaO-SiO_2 mixture was obtained by firing a mixture of CaCO_3 and SiO_2 (325-mesh quartz) in a molar ratio of 28.4:71.6 at 1200°C . Similar experiments were conducted with ternary mixtures of dolomite ($\text{MgCO}_3\cdot\text{CaCO}_3$), CaCO_3 and SiO_2 (325-mesh quartz) to mimic industrial float glass compositions but similarly limited reactions were observed (Figure 3). The results from both sets of samples was examined by X-ray analysis (XRD, XRG 3100, Philips, Natick, MA). XRD analysis was performed from $2\theta = 10^\circ$ to 70° with 0.04 step size and 2 second dwell time. Figures 4 and 5 show the powder X-ray diffraction patterns obtained from the $\text{Na}_2\text{O-SiO}_2$ eutectic and CaO-SiO_2 binary compound samples, respectively. The mixtures of soda ash and quartz form a homogeneous glass at each dwell time. The mixture of limestone and quartz shows that limestone converts to CaO by the dissociation of CO_2 . Two binary compounds, wollastonite ($\text{CaO}\cdot\text{SiO}_2$) and $2\text{CaO}\cdot\text{SiO}_2$ were formed, but the relative amounts of each phase did not change significantly with increasing dwell times at 1200°C . The majority of the pre-reacted batch remained as a mixture of $\text{CaO} + \text{quartz}$.

Task B. Low temperature reactions:

Prepared samples of commercial batch and samples prepared via Approaches I (selectively batch and pelletize) and II (pre-react to form binary compounds) will be heated to low temperature (over the range of 600°C to 1100°C) and time (from 0.25 to 24.0 hours on a non-linear time scale) to determine the low temperature segregation tendencies. It is proposed to use relatively large crucibles (10 cm diameter and 25 cm tall) to conduct the low temperature reactions.

The limited reactions at low temperatures that were evident from the previous task indicated that low temperature segregation was unlikely. An alternative approach was implemented to investigate potential segregation of the standard batch when melted. Two batches were prepared based on the formula used by Guardian Glass: a mixture of soda ash, limestone, and silica (NCS) and a mixture of soda ash, limestone, dolomite, and silica (NCDS) (Table I). Raw materials were mixed in a 3 l bottle by placing on a milling machine and the mixed samples were melted in 300 ml crucibles from 900°C to 1200°C in an electric kiln with dwell times, one and two hours. The samples were quenched in the air. After cooling, the sample was cut into two pieces vertically and one of the halves was cut into two pieces horizontally to separate top and bottom regions of

the sample. The both regions of the sample were observed using scanning electron microscopy (see Task D).

The melting behavior of the two batches was also studied using hot stage microscopy (HSM) (Misura 3, Expert System S.r.l, Modena, Italy). Samples were heated up to 1500°C with the heating rate of 20°C/minute. The side view of the samples was recorded from 500°C to 1500°C at every 10°C. The melting behavior of two batches is shown in Figures 6 and 7. NCS sample forms a sphere around 900°C and a semi-sphere around 950°C. Compared to NCS the melting of NCDS is slow. NCDS forms a sphere above 950°C and a semi-sphere around 1000°C. Height change of the samples with temperature as shown in Figure 8 confirms the slow melting behavior of NCDS.

Task C. High temperature reactions:

Prepare samples of commercial batch and samples prepared identically to those in Task B but fired over the temperature range of 1000°C – 1200°C to determine batch free time using established procedures.

To investigate the melting behavior of the pre-reacted batch materials, two initial sets of samples were prepared by mixing the Na₂O-SiO₂ eutectic with two different limestone and quartz intermediate materials: Set A with 325 mesh quartz and Set B with sand. The two intermediate materials (CaO-SiO₂ binary and Na₂O-SiO₂ eutectic) were mixed in 51.67:48.33 mole ratio to obtain a typical float glass batch composition. The final mixtures were dry ball milled for 15 minutes to homogenize the batches – the milling times were sufficiently short to not significantly alter the particle size. Eight 125 gram samples were weighed into mullite crucibles and heat treated to determine batch-free time – the time required to form a homogeneous glass without evidence of unreacted batch materials. Samples were placed in a gas-fired furnace pre-heated to 1400°C for times ranging from 30 minutes up to 240 minutes at intervals of 30 minutes. The sample from Set A produced a homogeneous glass in the first 30 minute dwell. Set B samples were batch-free after 90 minutes. The control mixed batch used by Guardian was batch free in 240 minutes.

Extrusion of pellets of selectively batched material were attempted, but the level of additives necessary, and general problems associated with extrusion, indicated that this approach was problematic and was subsequently abandoned. Spray drying, however, presented a clear opportunity for several reasons: finer grade quartz could be used, suspensions of the batch constituents (selectively blended) could be easily prepared, and a laboratory spray dryer was readily available. Therefore, three 25 volume percent slurries were prepared for spray drying: soda ash + quartz, limestone + quartz, and limestone + dolomite + quartz. These were prepared without any polymeric additives (dispersant or binders) to keep the materials as close to those used in industrial glass batches (and to avoid any potential problems with cost and oxidation state within the furnace). A 325-mesh (nominally 45µm) quartz was used and the limestone and dolomite, provided by Guardian Glass, were ground into finer powders before addition into the slurries. After 48 hours grinding, the specific surface area for limestone and dolomite were determined as 3.39 and 2.25 m²/g, respectively. The slurries were spray dried in a laboratory spray dryer (BE 985, Bowen Engineering, North Branch, NJ) under the conditions of inlet

temperature 145°C, and air pressure of 20 psi. In order to correct the control for the reduction in particle size, a second control formulation was made using 45 µm quartz.

To test the relative batch-free times, the pre-reacted, spray dried, and control formulations were evaluated at 1350°C, following the procedure detailed above. The spray dried materials (Approach I) of {Na₂CO₃+SiO₂} and {CaCO₃+MgCO₃·CaCO₃+SiO₂} were batch-free in 45 minutes at 1350°C and the pre-reacted materials (Approach II) of the same components were batch-free within 20 minutes at 1350°C. A standard control was batch-free time on the order of 240 minutes for coarse (350 mm) and 120 minutes with the fine (45 mm) quartz, demonstrating that the benefits are not simply an artifact of particle size (Figure 9). Compared to the current practice, Approach I reduced batch-free time by a factor of 5.3 (an 81% reduction) and Approach II yielded a reduction in batch-free time a factor of 12 (a 92% reduction). Similar results are observed for batches that are composed solely of soda ash, limestone, and quartz indicating a batch-free time reduction of 62% for reduced particle size and 12.5% for reduced particle size and selective batching, respectively.

Task D. Microstructural analysis:

Microstructural (via optical microscopy and SEM), phase (via XRD), and chemical (via SEM-EDS) analysis of the crucibles will be conducted to quantify the phase evolution and degree of segregation in samples prepared from Tasks B & C.

The micrographs obtained from the melted NCS samples are shown in Figures 10-13. At 900°C bottom region of the sample shows that most particles retain their shape. In the top region glass phase formed and covered unmelted particles. At 1000°C melting was further proceeded and lots of bubbles were shown in both regions of the sample. At 1100°C the glass phase increases in both regions, but some unmelted particles are imbedded in the glass phase. In the bottom region of the sample particles at the early stage of melting are shown. At 1200°C all the materials are mostly melted.

Figures 14-17 show the micrographs obtained from NCDS samples. At 900°C particles in the bottom region were connected by glass phase. In the top region more glass phase is shown around unmelted particles. At 1000°C most particles were melted in both regions, but some unmelted particles are shown. Unmelted particles are shown even in the samples prepared at 1200°C.

In an attempt to determine if segregation can be documented in a commercial melter, two samples were obtained (from the tank of the Guardian Glass plant in Geneva, NY) of unreacted material that floats on the molten glass and slowly reacts to produce batch-free glass. (These floating batch samples are commonly referred to as a “turtles.”). These samples were inspected visually, samples were collected from various locations and analyzed for mineralogy (using XRD), chemistry (ICP-AS analysis, Acme Analytical Labs, Vancouver, B.C.) and thermally (via simultaneous TGA-DTA). Overall, the results are essentially inconclusive, with only minor

composition variations observed, indicating a slight depletion of sodium, calcium, and magnesium, relative to the starting batch. This may be an indication of large scale (tens of centimeters) segregation.

Task E. Meetings:

Three meetings will be held (one at the beginning of the project, one at the middle-stage of the project, and one upon completion of the experimental portion of the project); DOE participation is invited.

The kickoff meeting was held in Fall 2002 at the Guardian plant in Geneva, NY. The second meeting was held in Winter 2003 with other representatives of the glass industry (GMIC) and the CGR (the NSF Center for Glass Research at Alfred University). The final meeting was held at Guardian Glass in May 2003 to explain the final results from this project and to discuss the feasibility of implementation on an industrial scale in future. Participants from Guardian Glass expressed great interests in the results proving the energy efficiency of the glass melting processes and possible reduction of environment emissions by selective batching. They are willing to support further studies by providing cost sharing through consultation, the supply of batch materials and the possibility of a pilot plant run after intermediate melter study.

4. Conclusions and recommendations for future work

Compiled results from this project demonstrate that dramatic reductions in the time required to form a homogeneous glass melt are realized by forcing alternative reaction paths during the initial stages of melting. Although this work is predicated on the idea of segregation of the batch on a gross scale during the initial stages of melting, demonstrating that segregation on a laboratory scale has been difficult. However, regardless of being able to demonstrate segregation, the selective batching approach has resulted in dramatic reductions in the time necessary to reach a batch-free state for a wide range of test conditions. These results indicate that both selective pre-reacting and selectively pelletizing (in the form of spray drying) can reduce the batch-free time by at least 80%.

Several tasks are recommended for further studies, and the details can be found in the pending proposal for a second phase study. The effect of quartz particle size and the role of flux size on batch free time should be determined. In this project the reduced particle size of batching materials resulted in the improved melting efficiency. However, the particle size range providing advantage in melting process should be defined with the competency of pelletizing technique. It is recommended to investigate how size of pelletized batch components impact melting efficiency. The variation in the size of pelletized components is expected to considerably influence the kinetics in melting process. The observations made during this project suggest that batches prepared using the selective batching technique also benefit from a reduction in bubble-free time. The treatments would be continued to determine the bubble-free times and evaluated for benefits correlating to the selective batching technique. Most importantly, intermediate-scale melting trials should be conducted to establish the benefits of selective batching technique on upscale. This will secure the possibility of trial runs for the implementation on an industrial scale.

Appendix A

Final Task Schedule

Final Task Schedule

Task	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
A	Binary reactions	8/9/02	8/9/02	11/30/02	100%	Completed.
B	Low temperature reactions	9/27/02	11/30/02	11/30/02	100%	Completed.
C	High temperature reactions	9/27/02	11/30/02	1/31/03	100%	Completed.
D	Microstructural analysis	10/18/02	11/30/02	12/31/02	100%	Completed.
E	Meetings	10/31/02	5/31/03	5/31/03	100%	Completed.
F	Reporting	10/31/02	7/31/03	7/31/03	100%	Completed.

Appendix B

Final Spending Schedule

Final Spending Schedule

Project Period:

10/01/02 to 06/30/03

Task	Approved Budget	Final Project Expenditures
Task 1 Binary reactions	9,000	9,000
Task 2 Low temperature reactions	13,000	13,000
Task 3 High temperature reactions	15,000	15,000
Task 4 Microstructural analysis	10,000	10,000
Task 5 Meetings	4,000	4,000
Task 6 Reporting	3,000	3,000
Total	54,000	54,000
DOE Share	40,000	40,000
Cost Share	14,000	14,000

Appendix C

Final Cost Share Contributions

Final Cost Share Contributions

Funding Source	Approved Cost Share		Final Contributions	
	Cash	In-Kind	Cash	In-Kind
CEER	10,000		10,000	
Guardian Industries		4,000		4,000
Total	10,000	4,000	10,000	4,000
Cumulative Cost Share Contributions				14,000

Appendix D

Energy Savings Metrics

One Unit of Proposed Technology:

The energy saving scenario uses a commercial float glass plant producing 700 tons/day of flat glass. A spray dried, selectively-batched raw material program is implemented.

One Unit of Current Technology:

The unit of current technology is a commercial float glass plant producing 700 tons/day of flat glass using conventional batching processes.

Discussion of Energy Savings:

In this scenario, the following assumptions are used:

1. The plant operates 365 days/year for a total annual production of 255,500 tons
2. The average specific energy use for melting, refining and forming is 8.6 million Btu/ton¹. This value is based on an average of actual measurements
3. The residence time of the melt in the tank is 60 hours (from batch charging to the forming process).
4. The estimated amount of energy that is required to keep the molten glass in the tank (beyond melting) is 1×10^5 Btu/ton/hour. This was estimated using the difference between the theoretic melting energy required and the actual energy used divided by average residence times in the tank (24 hours for container and 60 hours for flat glass).
5. Natural gas-fired furnace with an average fuel cost of \$5/MMBtu.

Using a spray dried, selectively batched material, we have shown that batch-free time can be reduced by at least 60% when particle size is not a factor. If the residence time is reduced by 60% to 24 hours rather than 60 hours, the estimated specific energy use for melting and refining would be 5.0 million Btu/ton, or a 40% reduction. If we estimate that the net reduction in energy after taking into account the increased energy for grinding and spray drying is 30%, the result is 6.0 million Btu/ton produced or a decrease of 2.6 million Btu/ton. If annual production is 255,000 tons, the annual energy savings would be 664 billion Btu, or \$3.3 million.

1. U. S. Department of Energy, Energy and Environmental Profile of the U.S. Glass Industry, Office of Industrial Technologies, 99 pp. 2002. 1999 estimates

Supplemental Tables and Figures

Table I. Compositions of Tested Batches

	Chemical Formula	NCS (w/o)	NCDS (w/o)
Soda ash	Na_2CO_3	22.65	20.38
Limestone	CaCO_3	6.90	6.20
Dolomite	CaMgCO_3		10.06
Sand	SiO_2	70.44	63.36

Table II. Batch formulae including Na_2CO_3 , CaCO_3 , $\text{CaCO}_3\text{-MgCO}_3$, and quartz. $\text{Na}_2\text{O-SiO}_2$ or Eutectic indicates the eutectic intermediate material between Na_2CO_3 and quartz. MCQ stands for the mixture of CaCO_3 , $\text{CaCO}_3\text{-MgCO}_3$, and quartz. Unreacted and reacted indicates intermediate materials fired at 1000°C and 1400°C , respectively. Fine and coarse in parenthesis indicates 325 mesh (45 μm) quartz and sand (325 μm) from Guardian Glass, respectively.

Batch	Description	Na_2CO_3	$\text{Na}_2\text{O-SiO}_2$	CaCO_3	$\text{CaCO}_3\text{-MgCO}_3$	CaO	CaO-MgO	Fine Quartz	Sand
A	Guardian standard batch (Coarse)	x		x	x				x
B	Guardian standard batch (Fine)	x		x	x			x	
C	Eutectic / Unreacted MCQ (Coarse)		x			x	x		x
D	Eutectic / Reacted MCQ (Coarse)		x			x	x		x
E	Eutectic / Unreacted MCQ (Fine)		x			x	x	x	
F	Eutectic / Reacted MCQ (Fine)		x			x	x	x	
G	Spray dried Guardian standard	x		x	x			x	

Table III. Batch formula including Na_2CO_3 , CaCO_3 , and quartz. $\text{Na}_2\text{O-SiO}_2$ or Eutectic indicates the eutectic intermediate material between Na_2CO_3 and quartz. CQ stands for the mixture of CaCO_3 and quartz. Unreacted and reacted indicates intermediate materials fired at 1000°C and 1400°C , respectively. Fine and coarse in parenthesis indicates 325 mesh quartz and sand from Guardian Glass, respectively.

Batch	Description	Na_2CO_3	$\text{Na}_2\text{O-SiO}_2$	CaCO_3	CaO	Fine Quartz	Sand
H	Alfred standard batch (Coarse)	x		x			x
I	Alfred standard batch (Fine)	x		x		x	
J	Eutectic / Unreacted CQ (Coarse)		x		x		x
K	Eutectic / Reacted CQ (Coarse)		x		x		x
L	Eutectic / Unreacted CQ (Fine)		x		x	x	
M	Eutectic / Reacted CQ (Fine)		x		x	x	
N	Spray dried Alfred standard	x		x		x	

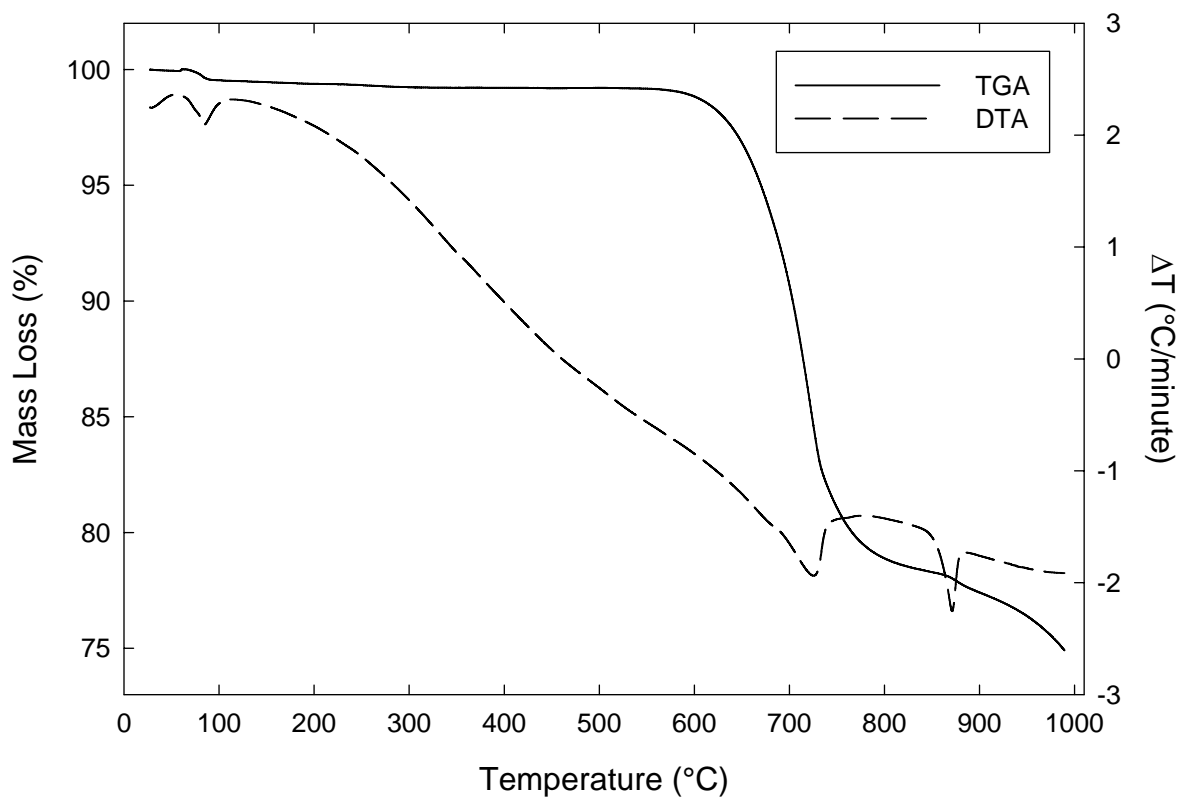


Figure 1. DTA-TGA curves for the mixture of Na_2CO_3 and CaCO_3 in a 1:1 molar ratio. Three endothermic peaks are seen at 85.5°C, 725.6°C, and 871.3°C due to the dehydration, eutectic liquid formation, and loss of CO_2 , respectively.

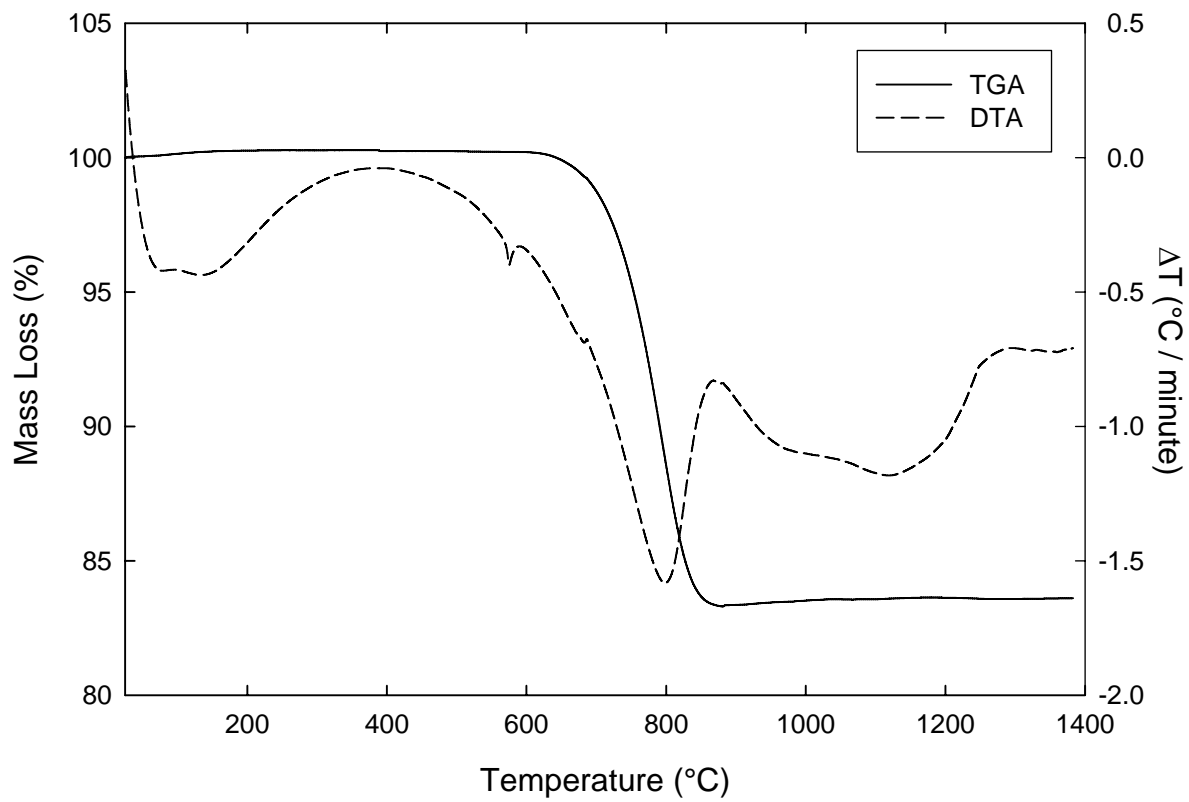


Figure 2. DTA-TGA curves for the mixture of Na₂CO₃ and SiO₂ in a 74:26 molar ratio.

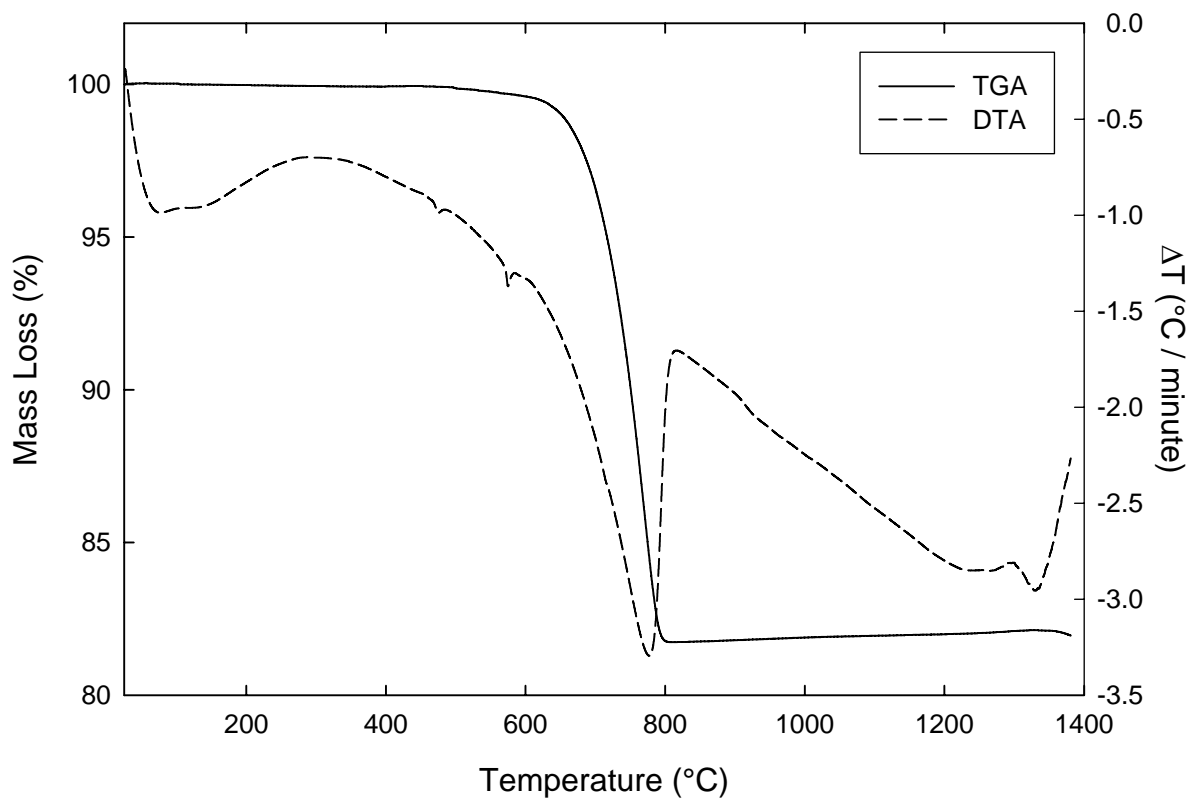


Figure 3. DTA-TGA curves for the mixture of $\text{CaCO}_3 + \text{CaCO}_3 \cdot \text{MgCO}_3 + \text{SiO}_2$ in a 9.45:12.34:78.21 molar ratio.

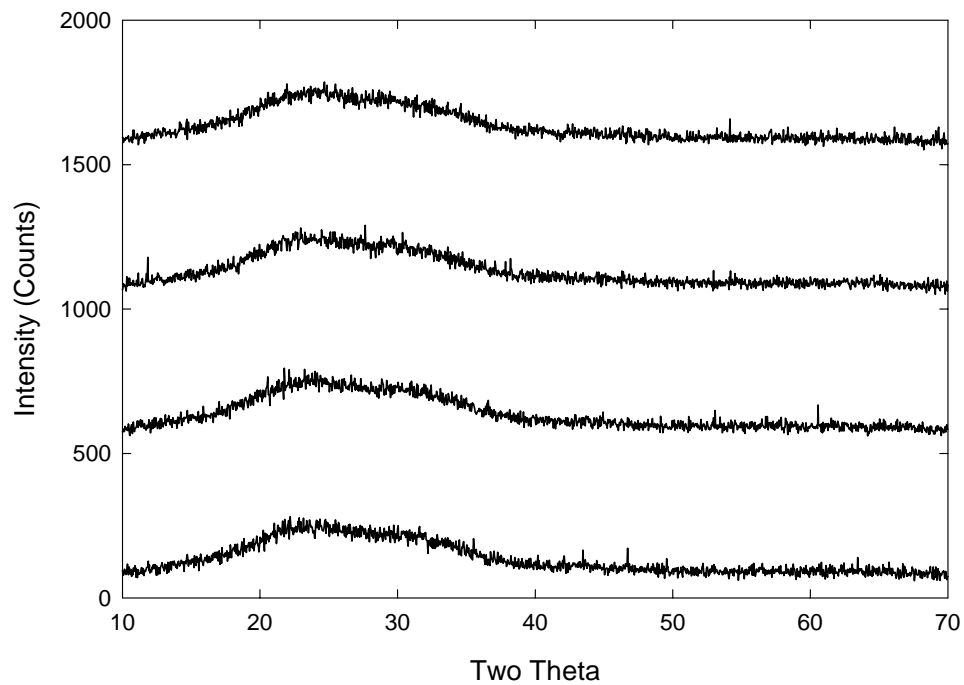


Figure 4. XRD analysis on the intermediate material made of soda ash and quartz. Dwell time changes from 2 to 8 hours from bottom to top by 2 hour steps. Amorphous $\text{Na}_2\text{O-SiO}_2$ was formed in all samples.

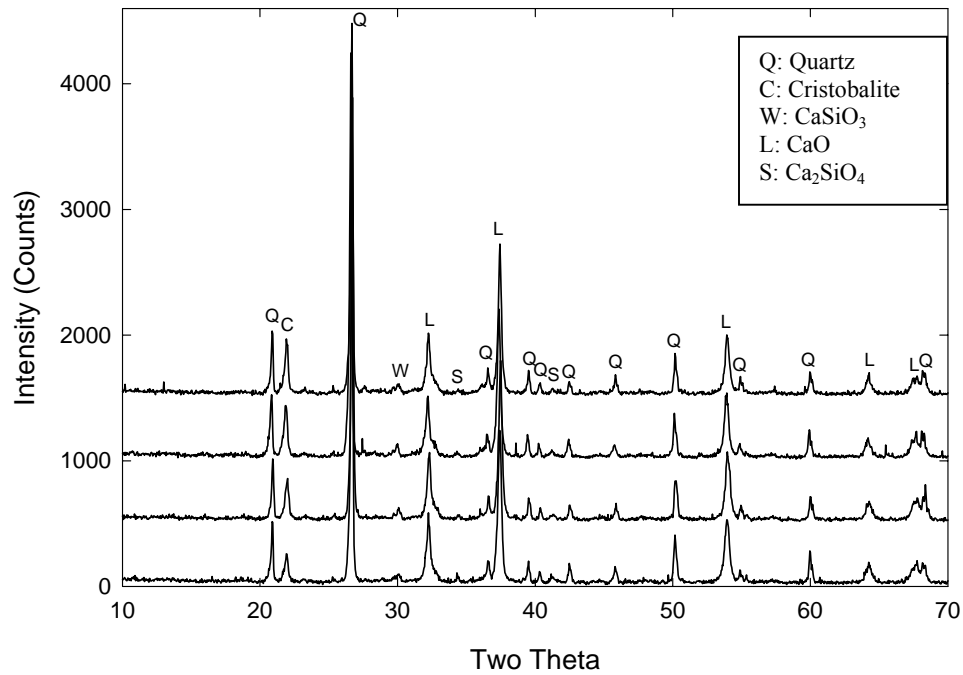


Figure 5. XRD analysis on the intermediate material made of limestone and quartz. Dwell time changes from 2 to 8 hours from bottom to top by 2 hour increments. Limestone becomes CaO by the dissociation of CO₂. The interaction between CaO and quartz forms CaO·SiO₂ and 2CaO·SiO₂.

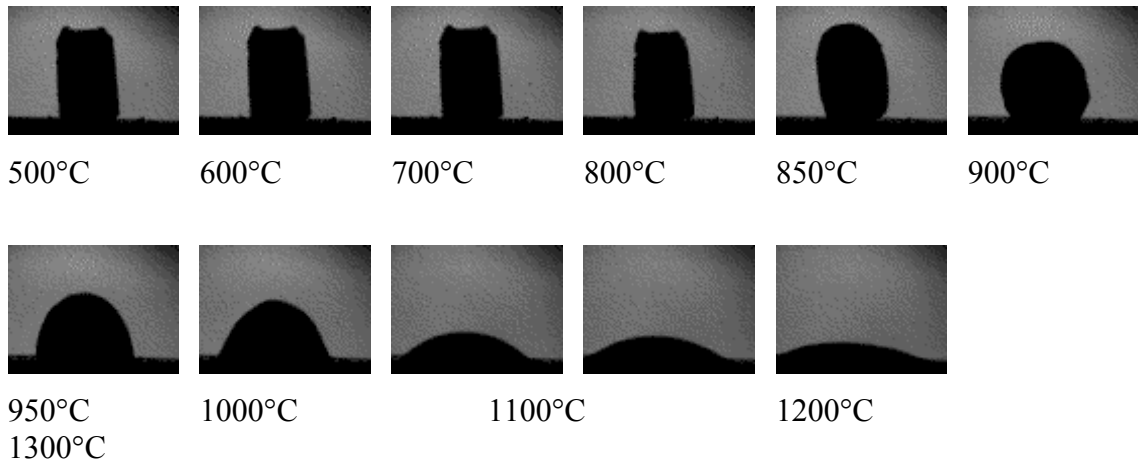


Figure 6. Melting behavior of NCS sample.

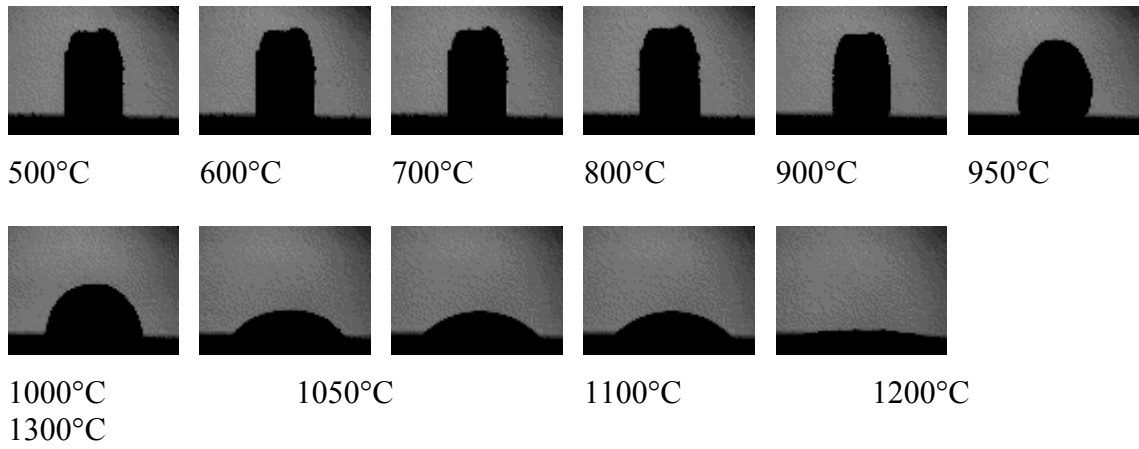


Figure 7. Melting behavior of NCDS sample.

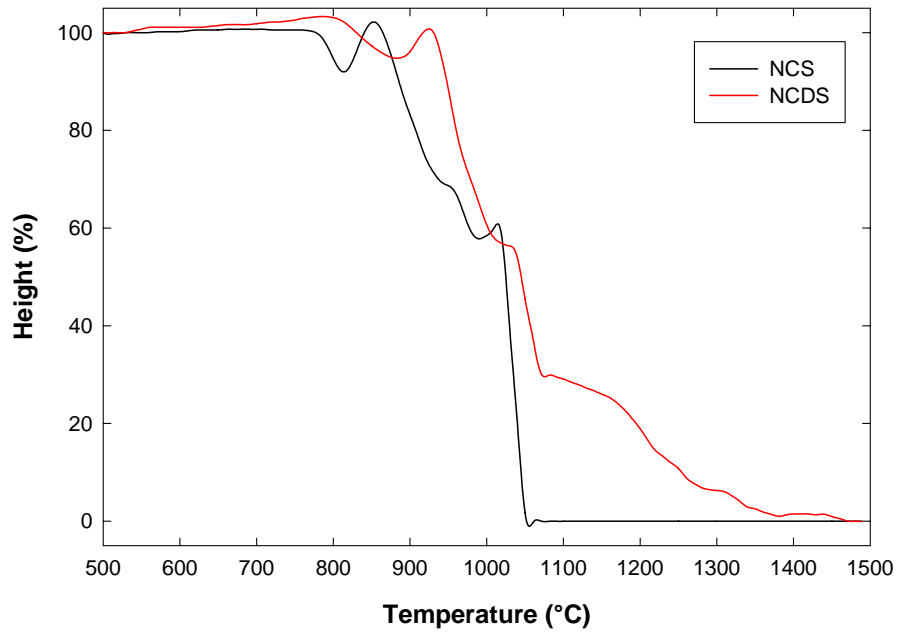


Figure 8. The height change of NCS and NCDS samples with temperature.