

Alumina and Silica Sources for E-Glass Fiber Manufacturing – Melting Energy Aspect

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Abstract

Two major sources of alumina are used in commercial production of E-Glass fibers for reinforcement of plastic materials. Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is the most common alumina source for preparing E-Glass batch. The $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of kaolinite is 1:2. Pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, is also used by some of fiber glass producers in Asia, which has an $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of 1:4. In some cases, kaolinite and pyrophyllite are also used for preparing E-Glass batches. The use of pyrophyllite or the mixture of pyrophyllite and kaolinite enables the elimination of sand in the batch, which improves batch-to-melt conversion efficiency and lowers conversion energy. This research focuses on the calorimetric and kinetic characterization of kaolinite and pyrophyllite-derived batch melting and intermediate phase formation. Energy of batch-to-melt conversion and batch-free time of the two types of batch materials with and without sand, are discussed.

I. Introduction

Pyrophyllite, “fire-leaf” in Greek, is a natural mineral formed from the reaction of kaolin (aluminosilicate) and quartz (silica) in geological events millions of years ago. Pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, structurally contains one molecule of alumina (Al_2O_3) for every four molecules of silica (SiO_2). In the Asia Pacific region, pyrophyllite is one of the key batch ingredients for E-Glass fibers [1]. The use of pyrophyllite as a sole source of Al_2O_3 and SiO_2 for E-Glass fiber making started in Japan decades ago, later practiced in South Korea and now made in China. Limited use of pyrophyllite in E-Glass fiber production has also been reported in South America. However, global production of E-Glass fibers mostly use kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as a source of Al_2O_3 and a part of SiO_2 input, for which Al_2O_3 to SiO_2 ratio is 1:2. Besides the differences in Al_2O_3 and SiO_2 between the two minerals, pyrophyllite contains less chemically bonded water than kaolinite—about 50% to 75%. Furthermore, the former is hydrophobic: whereas, the latter is hydrophilic.

The use of pyrophyllite can lead to the complete removal of silica sand from the E-Glass batch; hence, provide the benefit of batch melting energy savings as discussed in this article. However, import of the mineral from the Asia Pacific region is cost prohibitive, so its use has not been widely adopted in Europe or North America where commercial-grade kaolinite is abundantly available.

A global mineral geographical survey (Table 1) shows that pyrophyllite production between 2007 and 2010. Although most pyrophyllite minerals are prepared to meet ceramic industry needs there should be sufficient resources for fiber glass, particularly for E-Glass fibers. One of the key requirements for the fiber-grade pyrophyllite products is that Al_2O_3 content should be greater than 17 wt%. In addition, the product $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio and impurity iron (Fe_2O_3) should be kept stable. In the author’s opinion, a lack of awareness of pyrophyllite benefit for E-Glass fiber making may be one of the key factors that hinder the mining industry from exploring its business potential for the fiber glass industry. In this article, the author intends to share results from a set of technical studies, which convincingly demonstrate the benefits of utilizing pyrophyllite as a low-energy batch ingredient when making E-Glass fibers.

The batch melting study to address industrial applications and questions can be reduced to a scaling problem depending on batch size – from industrial scale in tons to atomic laboratory scale in milligrams [3]. In this study, batch reaction and melting were studied using samples in a laboratory batch size range from milligram to kilogram. At a milligram level, energy of batch-to-melt conversion can be accurately determined using a high temperature differential scanning calorimeter/thermal gravimetric analyzer (DSC/TGA). At a kilogram level, the kinetics of the batch-to-melt conversion process in a gas-fired furnace can be monitored, which is closer to the combustion environment of a commercial furnace operation. At an intermediary level between the two levels, by heat treating samples in a joule-heated box furnace to selected temperatures, one can examine intermediate phase formation and temperature at which the batch becomes completely glassy. Combining results from the studies, key conclusions on how major raw materials affect batch-to-melt process in terms of melting rate and required energy in a commercial furnace operation can be reached.

II. Experimental

Batch mixtures were prepared using appropriate amounts of commercial E-Glass grade pyrophyllite, kaolinite, sand, limestone, colemanite, plus small amounts of fining agent and rouge (actual formulations are PPG proprietary information). Pyrophyllite, kaolinite, and sand have the same particle size range with about 90% passing through a 325 mesh sieve and 100% passing through a 60 mesh sieve. For simplicity throughout the text, *Py-batch* stands for batch containing pyrophyllite without sand and *KS-batch* stands for batch containing kaolinite and sand.

Netzsch Model DSC5 (Netzsch Instruments, Germany) was used to collect energy output during batch-to-melt conversion process. The sample was heated at a rate of 10°C/min from 22°C to 1400°C. Prior to each test, the instrument was calibrated using standards of indium, gold, aluminum, and zinc. Alumina pans were used for both sample and reference; the accuracy of the results was established to be within $\pm 2^\circ\text{C}$.

A custom built, thermal gravimetric analysis (TGA) unit was used to compare fusion losses between the Py- and KS-batches, which enabled batch size increases by 5,000X from less than 5 mg to 25 g. This process permitted results that were more representative to actual glass yield in commercial production scale although the melting temperature and atmosphere of commercial operation were different. In the test, a 25 g batch was placed into a Pt-crucible and the crucible was suspended through a Pt-rod in the center of a joule heated box furnace (DELTECH INC., Denver, CO) to keep temperature uniform throughout the test. The other end of the suspension rod was mechanically connected with an exterior digital scale on the top of the furnace. The scale was placed on a device that damps the ground vibration and was connected with a computer for automatic sample weight recording. The data collection was set at a 1-minute duration per collection. For both samples, the furnace was preheated to 600°C, heated to 1450°C at rate of 100°C/h, and then kept at 1450°C overnight.

Isothermal heat treatment was performed on pure pyrophyllite, kaolinite, Py-batch, and KS-batch. The raw material and batch reactions were conducted between 300°C and 1500°C. The samples, about 20 g each, were held at a given temperature for one hour, then immediately cooled in air by taking them out of the furnace at the set temperature. The treated samples were ground to fine powder and analyzed by using an X-ray diffraction (XRD) analysis method. The PANalytical X'Pert MPD X-ray diffractometer (Westborough, MA) was used to collect data under the following instrumental settings: 2θ scan range from 10° - 75°, a step size of 0.05° and 10 second per step, Cu anode at 40 kV/50 mA, 0.04° soller slit, 1° divergence slit, and 0.10 mm receiving slit.

For the gas-fired furnace batch test, batches were prepared, melted, and evaluated at the same time. Each batch pile, approximately 1.2 kg, was placed in a flat high-silica tray and subsequently transported into the furnace preheated at 1350°C. The temperature setting was based on the glass melt viscosity at 10 Pa·s (100 Poise). A gas-fired flat flame burner was placed on top of the furnace roof and fired towards the batch samples. Images of batch melting were collected using a 20X zoom digital camera through the furnace front door window. Figure 1 shows the furnace, its control system, and starting configuration of the batch pile.

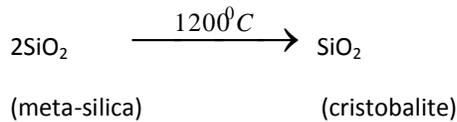
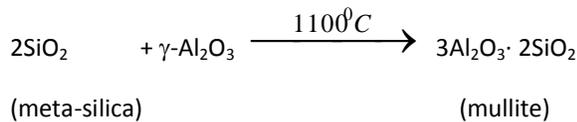
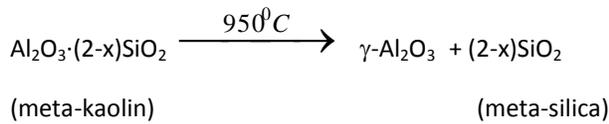
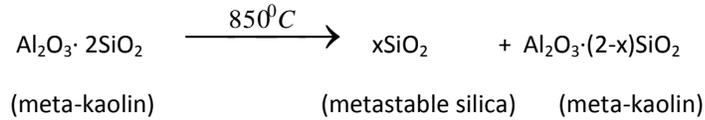
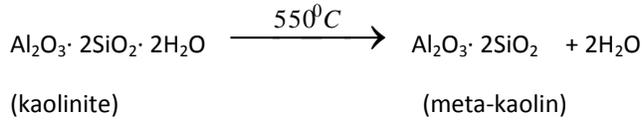
III. Results and Discussion

Figure 2 shows DSC spectra (specific heat vs. temperature) and calculated energy (integrated area under the DSC curve) required for heating pyrophyllite and kaolinite, respectively, from room temperature to 1400°C. An endothermic reaction for kaolinite is peaked at ~550°C, which corresponds to dehydroxylation or removal of chemically-bonded water species, plus simultaneous transformation from crystalline kaolinite to amorphous meta-kaolin (more discussions detailed later). On the other hand, a broad endothermic reaction for pyrophyllite peaked at ~750°C, which corresponds to removal of chemically-bonded water species without any phase transformation. A small exothermic band at ~1000°C suggests crystalline phase formation from amorphous meta-kaolin (more discussion detailed later). The DSC-derived energy calculation shows that pyrophyllite consumes slightly less energy than kaolinite, which is primarily related to the evaporation of different amounts of water from the materials.

Figure 3 shows DSC spectra and DSC-derived energy of batch-to-melt conversion for Py- and KS-batch, respectively, from room temperature to 1400°C. A small endothermic reaction that peaked at ~150°C from KS-batch was assigned to the evaporation of surface-absorbed moisture water on kaolinite. The endothermic band between ~350°C and ~400°C was associated with removal of chemically-bonded water species from colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$. Both batches exhibited an endothermic band at ~550°C as a result of the chemically-bonded water removal from either kaolinite or pyrophyllite. However, the endothermic band at ~450°C for the KS-batch was also related to the evaporation of the chemically-bonded water species. It follows that two types of structural waters exist in the kaolinite, which have different bonding energies with silicate lattice or network. The endothermic bands peaked at ~750-800°C resulting from the decomposition of limestone (CaCO_3) from both batches. A small, broad endothermic band centered at ~950°C can be assigned to the formation of intermediate silicate phases. The small peak or shoulder at ~1050°C corresponds to the dissolution of residual silica in the batches (small amounts of quartz exist in pyrophyllite). Finally, at ~1080°C, the conversion of the reacted batch mixture to melt started. Above 1080°C, the shape of the DSC spectra suggested that the rate of melting was faster for the Py-batch than KS-batch.

Figure 4 illustrates batch weight loss during the batch-to-melt conversion process for Py-batch and KS-batch. The rapid data sampling plan enabled the test to capture most of initial sample weight losses from evaporation of the bonded water from pyrophyllite, kaolinite, and colemanite. The starting temperature was sufficiently lower than the limestone decomposition temperature and the temperature of the boron evaporation from colemanite. The results showed that the Py-batch had about 12% lower fusion losses than the KS-batch. Since the amount of limestone and colemanite in the two batches were the same, the relative difference can only be attributed to amounts of chemically-bonded and surface-absorbed moisture water in pyrophyllite and kaolinite.

Figure 5 shows XRD analysis of kaolinite and pyrophyllite with and without heat treatment. For kaolinite, the absence of XRD peaks for the kaolinite crystalline phase after heat treatment between 625°C and 650°C (Figure 3a) can be attributed to meta-kaolin formation as a result of the removal of chemically-bonded water species. Meta-kaolin is amorphous at a macroscopic scale. The phase transformation can be described according to [4,5]:



The amorphous meta-kaolin is a precursor of mullite ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) once meta-kaolin is heated to a higher temperature. XRD analysis showed that both mullite and tridymite increase when kaolinite is heated at 1200°C or higher (Fig. 5a). XRD analysis also showed that samples contain small amounts of rutile, which is a known impurity in kaolinite.

On the other hand, as shown in Fig. 5b, pyrophyllite remains in its crystalline structure before and after heat treatment. A significant amount of mullite formed in the heat-treated pyrophyllite only between 1200°C and 1300°C and then remained at a minimum between 1400°C and 1450°C. Cristobalite, however, increased significantly. The reaction can be explained in terms liberation of cristobalite in literature [5,6].

It should be noted that in actual heat-treated E-Glass batch samples with little sodium and abundant calcium, intermediate silicate phases do not match with mullite, suggesting that a reaction of calcium prevents the reacted batches from forming mullite or aluminosilicate phases – independent of batch types containing pyrophyllite or kaolinite and sand. Table 2 summarizes the separate results of XRD analysis for both batches heat treated over temperatures between 200°C and 1500°C. The as-prepared batches were also analyzed and included for comparison. The last crystalline phase dissolved during the batch-to-melt conversion was cristobalite (SiO_2) independent of batch type. On the other hand, the high temperature DSC study showed that batch using pyrophyllite without sand can accelerate batch melting rate and hence require less energy during the batch-to-melt conversion process.

The batch melting rate or batch-free time was determined for the two types of E-Glass batches at 1350°C by visually monitoring the batch pile melting progress as illustrated in Figure 6. Noticeably, without sand in the batch, Py-batch melted significantly faster than KS-batch. The relative melting rate difference between the two types of batches was about 15%, knowing the batch-free times were about 25 and 30 minutes for Py- and KS-batch, respectively. The results support the high-temperature DSC finding discussed previously.

Combining high-temperature DSC results with observations from batch melting tests using a gas-fired furnace, one can conclude that the use of pyrophyllite in E-Glass batch can remove sand; therefore, provide benefit in accelerating the batch-to-melt conversion process. In turn, the associated energy can be potentially saved. Based on the DSC measurements, the energy saving is about 1550 kJ/kg-glass. It translates to approximately 66 million BTU annual saving of natural gas for a commercial-scale furnace producing 45,000 MT of E-Glass fibers.

IV. Summary

A comprehensive laboratory study was performed to assess potential benefit of utilizing pyrophyllite in E-Glass batch with a complete removal of sand. The study covered measurements of batch-to-melt conversion energy by the DSC method, fusion loss by the TGA method, the intermediate phase formation in batch reaction by heat-treatment and XRD analysis methods, and batch-free time by using a gas-fired furnace. Combining results from the above investigations, the conclusion is reached that the use of pyrophyllite in E-Glass batch without the addition of sand can increase glass yield by about 12% and reduce energy consumption during the batch melting by 1,550 kJ/kg-glass as compared to E-Glass batch using kaolinite and sand. The use of pyrophyllite for E-Glass and perhaps other commercial silicate glass products provides the glass industry a solution for energy efficiency and a cleaner environment for the fiber glass and glass industry. A review of literature on the global source of pyrophyllite suggests that sufficient repositories exist world wide for future E-Glass fiber production should the mining industry realize its potential and these new business opportunities.

Acknowledgement

Author thanks Fiber Glass Science and Technology, PPG Industries, Inc. for supporting the study and survey of selective pyrophyllite mining sites. Batch tests and related characterizations supported by R. Hicks, CM. Dai, L. Rukavina, and Dr. M. Reben are acknowledged.

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Table 1. Global Mineral Survey of Pyrophyllite and Talc Production (Unit: metric tons) [2]

Region, Country	2007	2008	2009	2010	Region, Country	2007	2008	2009	2010
World Total	1,820,000	1,570,000	1,410,000	1,500,000					
Asia Pacific					Mid East				
Australia	1,200	1,200	1,200	1,200	Egypt	67,000	69,000	72,000	75,000
China	2,000,000	2,200,000	2,300,000	2,000,000	Turkey	12,722	3,364	6,887	8,000
India	87,000	87,000	88,000	87,000	North America				
Japan	345,000	350,000	340,000	340,000	Canada	79,000	70,000	44,000	96,000
Pakistan	32,675	33,000	3,500	34,000	US	769,000	706,000	511,000	604,000
South Korea	798,054	892,625	617,411	700,000	South America				
Thailand	415,420	106,600	200,000	200,000	Argentina	24,836	22,218	22,894	23,000
Europe					Brazile	401,204	401,210	401,300	410,000
Finland	550,000	550,000	500,000	500,000	Peru	13,925	14,733	14,750	14,800
France	420,000	420,000	420,000	420,000	Paraguay	200	200	200	200
Italy	140,000	140,000	140,000	140,000	Africa				
Russia	170,000	160,000	160,000	160,000	South Africa	123,573	80,704	114,889	122,511
United Kingom	6,000	6,000	6,000	6,000	Uruguay	1,150	1,150	1,150	1,150

Note – values in italic font include pyrophyllite, talc, and possible other related minerals.

Table 2. XRD Phase Analysis of Heat-Treated E-Glass Batches

Heat Treatment	Py-Batch	KS-Batch	Heat Treatment	Py-Batch	KS-Batch
RT-300°C	Pyrophyllite	Clay	800°C	Pyrophyllite	
	Silica	Silica		Silica	Silica
	Limestone	Limestone		Ca-silicate	Ca-silicate
	Colemanite	Colemanite		Ca-borate	Ca-borate
400°C	Pyrophyllite	Clay	900°C	Anorthite	
	Silica	Silica		Pyrophyllite	
	Limestone	Limestone		Silica	Silica
	Colemanite*	Colemanite*		Ca-silicate	Tricalcium silicate
500-600°C	Pyrophyllite	Silica	1000°C	Ca-borate	Ca-borate
	Silica	Silica		Anorthite	
	Limestone	Limestone		Wollastonite	
	Anorthite	Colemanite*		Silica	Silica
	Colemanite*	Colemanite*		Wollastonite	Ca-silicate
700°C	Pyrophyllite				Ca-borate
	Silica	Silica	1100°C	Silica	Silica
	Limestone	Limestone	1200-1500°C	Glass	Glass
	Anorthite				
	Ca-silicate	Ca-silicate			
	Ca-borate	Ca-borate			

*dehydrated borate phase.

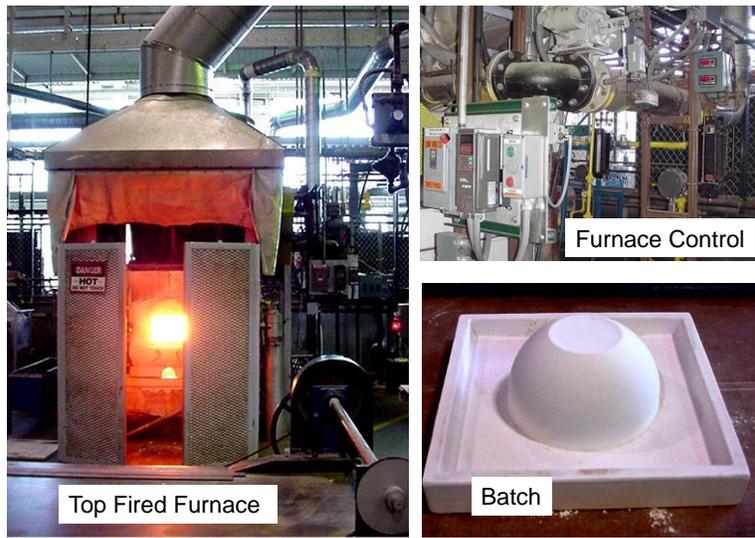


Figure 1. Batch test using natural gas fired furnace (PPG, Industries, Inc.)

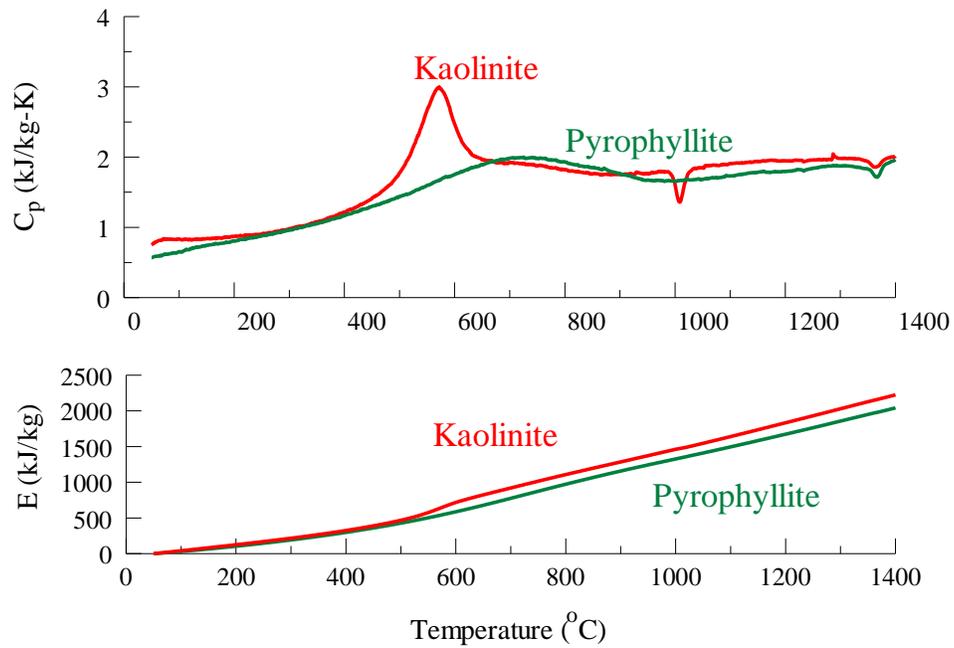


Figure 2. High temperature DSC spectra of pyrophyllite and kaolinite (top) and calculated energy (bottom) as a function of temperature.

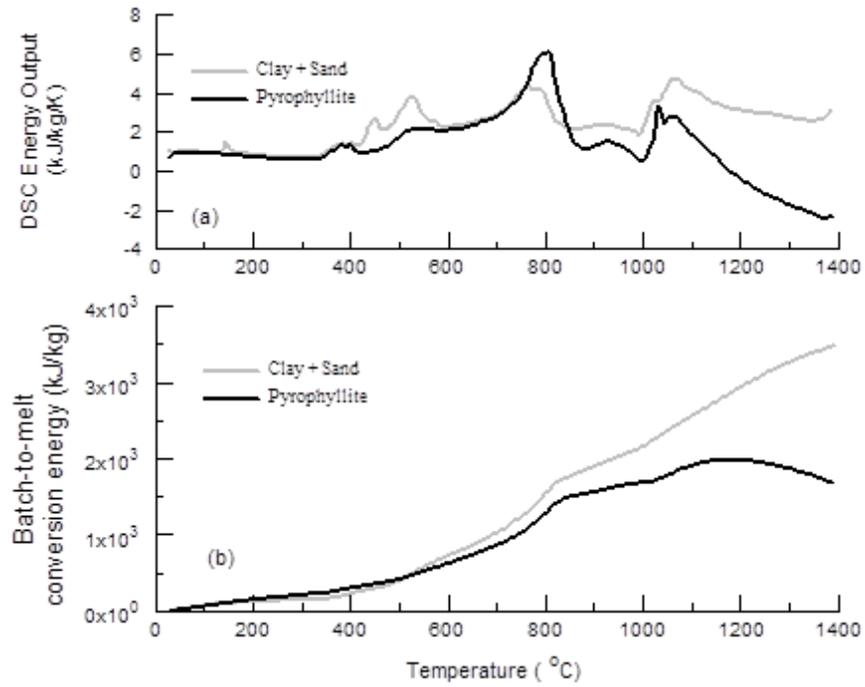


Figure 3. High temperature DSC Spectra (top) and calculated energy (bottom) for batches as a function of temperature.

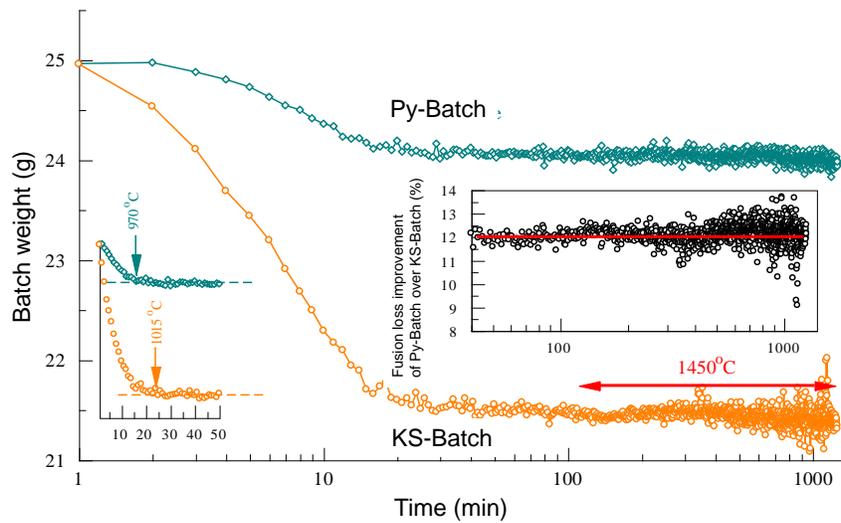


Figure 4. Batch fusion loss test, illustrating 12% glass yield improvement obtained using Py-Batch (Pyrophyllite Batch) over KS-Batch (Kaolinite-Sand Batch).

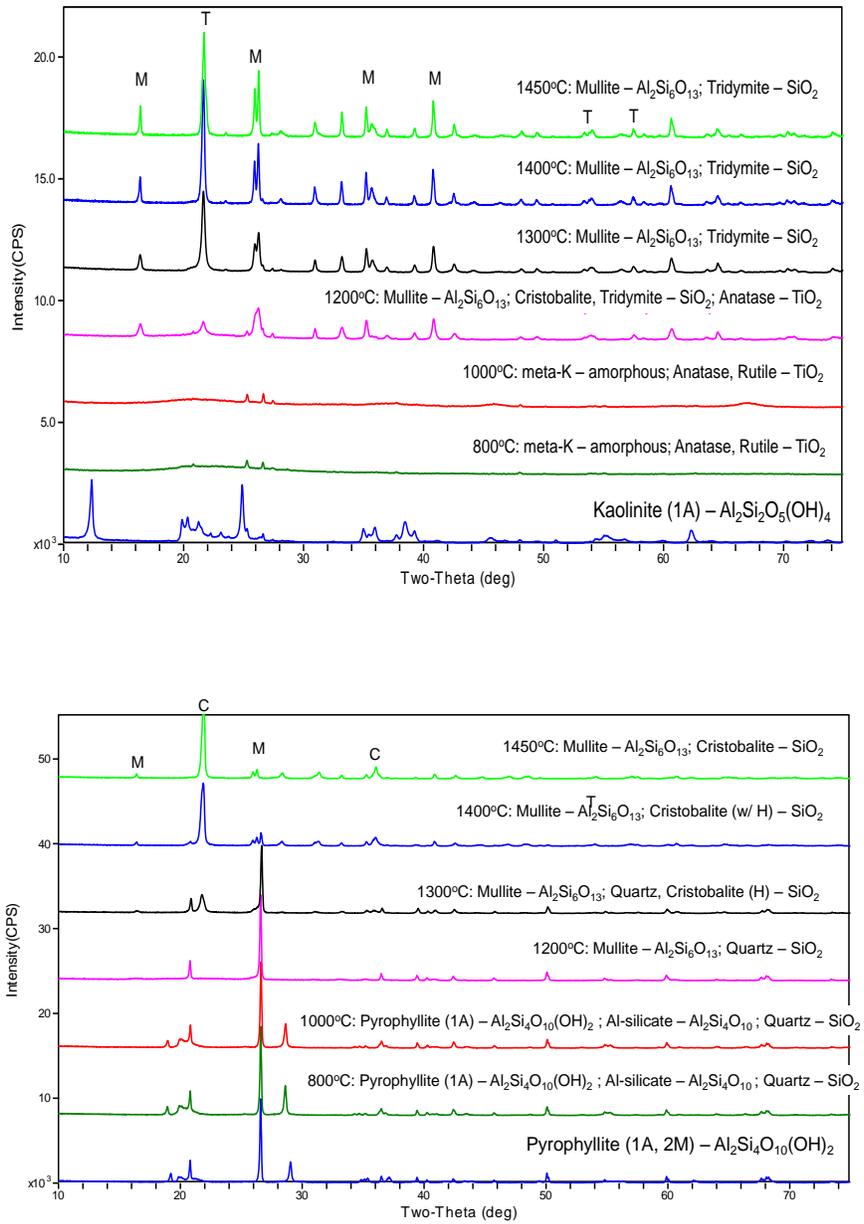


Figure 5. Powder XRD analysis of kaolinite (top) and pyrophyllite (bottom) with and without heat-treatment.

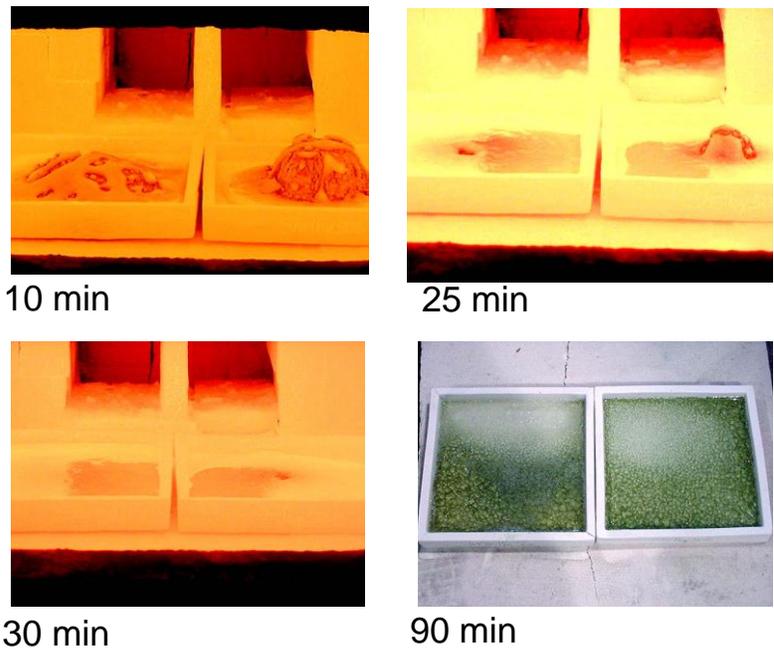


Figure 6. Photomicrographs illustrating difference in kinetics of batch-to-melt conversion process at 1350°C, plus final glass made, using E-Glass batches containing pyrophyllite (left on each photo) and kaolinite – sand (right on each photo).