

Non-equilibrium melting processes of silicate melts with different silica content at low-temperature plasma

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Abstract. This article is devoted to research the possibility of high-temperature silicate melts producing from different silica content at low-temperature plasma taking into account non-equilibrium melting processes.

1. Introduction

Silicate melting using strong plasma flows is a high-tech process that provides processing of both man-made and natural raw materials. The use of low-temperature plasma (LTP) for the production of high-temperature silicate melts is connected with high temperatures produced by plasma generator much higher than melting temperatures of all silicate materials. This creates consistently high temperatures and energy concentration allowing the transition of processed materials to a molten state. In melting silicate systems using the low-temperature plasma, a range of diverse physicochemical and phase transformations occur, the intensification of which is increased with the increase of temperature.

The original materials for the production of high-temperature silicate melts were as follows:

- Ash from Seversk (Tomsk region, Russia) obtained after coal burning;
- oil shale combustion products from Province Dalian (China).

The chemical composition of these raw materials is presented in Table 1.

Table 1. The chemical composition of original raw materials before plasma treatment.

| Raw materials | Oxide content, (wt. %) | | | | | | | |
|-------------------------------|------------------------|------------------------------------|------------------------------------|------------|------------|-----------------------|------------|-------|
| | <i>SiO₂</i> | <i>Al₂O₃</i> | <i>Fe₂O₃</i> | <i>CaO</i> | <i>MgO</i> | <i>K₂O</i> | Δm | M_K |
| Ash | 51.16 | 35.07 | 3.62 | 8.33 | 0.91 | 0.23 | 0.68 | 9.33 |
| Oil shale combustion products | 61.59 | 23.36 | 7.91 | 1.60 | 1.27 | 1.34 | 2.93 | 29.60 |

$$\Delta m - \text{weight loss, } M_K - \text{acidity index, } M_K = \frac{SiO_2 + Al_2O_3}{CaO + MgO}$$

According to Table 1, the raw materials contain over 50% of SiO₂, which is the main glass former. The acidity index of the used anthropogenic waste is significantly higher than that of the traditional silicate raw materials. The high acidity index has a positive effect on the chemical and thermal resistance of the finished articles. A tendency to crystallization increases with the decrease of the acidity index, and durability decreases.

2. Experimental work

The melting process of raw materials was experimentally carried out in the electro-plasma apparatus for manufacturing a refractory silicate melt [5]. The plasma-supporting gas flows out of the discharge



jet of the electro-plasma apparatus and serves as a heating material. The LTP jet enters the water-cooling melting furnace to perform melting of the refractory silicate raw material.

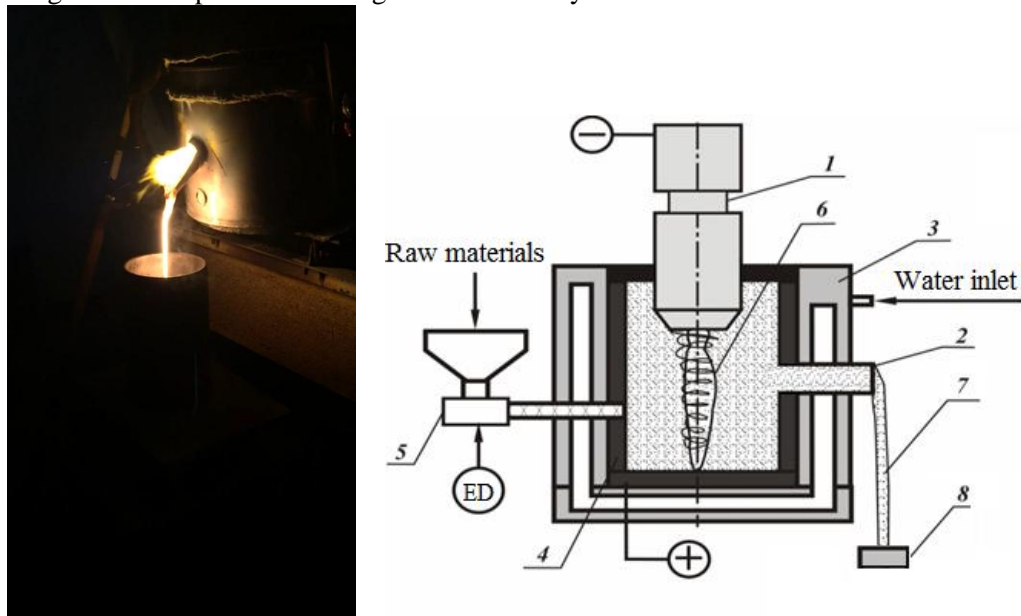


Figure 1. Experimental electro-plasma apparatus for mineral fiber production:
1 – plasma torch; 2 – pouring hole; 3 – water-cooled melting furnace; 4 – graphite electrode; 5 – worm feeder; 6 – plasma jet; 7 – melt; 8 – mold

Operation of the electric-plasma apparatus is based on the interaction between highly concentrated plasma flows and a raw material. Plasma torch 1 is placed in melting furnace equipped with pouring hole. Graphite electrode is installed in the bottom of melting furnace and connected with the positive pole of DC power supply (anode), while the plasma torch is connected with its negative pole (cathode). Once silicate melt reaches the level of the pouring hole, it will be discharged through it into forming hood. By means of batcher mounted into worm feeder 6 driven by electric drive, powder raw material is fed to the melting furnace. Plasma jet is projecting between plasma torch and graphite electrode. A raw material starts to melt and homogenize under a strong thermal effect (3000-5000 °C). The raw material particles are then mixed with a high-temperature silicate melt and melted uniformly. Furthermore, this method of feeding of raw materials makes possible to avoid a loss of fine particles blowing by a LTP jet. This method provides a uniformity and viscosity of low melt within the whole volume of the melting furnace.

It is advisable to identify the behavior of silicate systems under the equilibrium conditions using the state diagram and melting curves reflecting the quantity and composition of the liquid phase at temperature changes [1-4]. The analysis of the equilibrium processes for recalculation to a ternary system showed that the temperature required for the production of 100% melt ranges between 1640-1700°C depending on SiO₂ contained in the raw material.

A study of melting processes of silicate raw materials comprising 50-65% silica includes the analysis and comparison of equilibrium and non-equilibrium processes of the formation of silicate melt mixtures having different SiO₂ content.

3. Results and discussion

The analysis of melt formation based on the actual chemical composition (Table 2) shows that the primary melt is formed at 1170 °C, and comes to 33.33%. These processes are non-equilibrium and reflect the traditional material melting in tanks at running heating rates.

Table 2. The melt amount produced by ash fusibility depending on eutectics melting.

| System | Composition, (wt. %) | Temperature, (°C) | Eutectic melt, (%) | Total melt amount, (%) |
|--|-------------------------------------|-------------------|--------------------|------------------------|
| CaO-Al ₂ O ₃ -SiO ₂ | SiO ₂ – 55 | 1170 | 33.33 | 33.33 |
| | Al ₂ O ₃ – 37 | | | |
| | CaO – 8 | | | |
| FeO-SiO ₂ | SiO ₂ – 38 | 1178 | 4.99 | 38.32 |
| | FeO – 62 | | | |
| MgO-Al ₂ O ₃ -SiO ₂ | MgO – 21 | 1355 | 3.90 | 42.22 |
| | Al ₂ O ₃ – 22 | | | |
| | SiO ₂ – 47 | | | |
| CaO-MgO-SiO ₂ | SiO ₂ – 43,6 | 1400 | – | – |
| | MgO – 9,2 | | | |
| | CaO – 47,2 | | | |
| CaO-SiO ₂ | SiO ₂ – 63 | 1436 | – | – |
| | CaO – 37 | | | |
| CaO·Al ₂ O ₃ ·2SiO ₂ (anorthite) | | 1450 | – | 52 |
| MgO-SiO ₂ | SiO ₂ – 65 | 1543 | – | – |
| | MgO – 35 | | | |
| Melting due to dissolution Al ₂ O ₃ и SiO ₂ | | 1550 | – | 82 |
| Complete melting | | 1590 | – | 100 |

Melting of eutectic comprising 38% of SiO₂ and 62% of FeO, occurs at 1178 °C with the formation of 4.99% of the eutectic melt. Further, the melt is formed due to bonds between MgO and SiO₂ at 1355 °C, the total melt amount is 42.22%. At the further temperature increase, the melt is formed not due to eutectics, but rather anorthite melting and dissolving of silica and aluminum. At temperature of 1590 °C, ash will be completely fused.

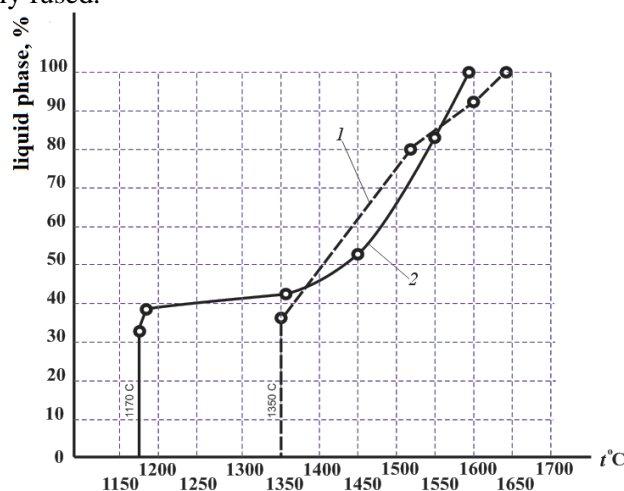


Figure 2. Ash fusibility curves:
1 - equilibrium dependence in CaO-Al₂O₃-SiO₂ system;
2 – non-equilibrium dependence of the actual chemical composition.

The analysis of ash fusibility curves (Fig. 2) shows that the starting temperature of melt formation does not exceed 1350 °C. The same amount of primary melt (approx. 35%) in the real system is formed at 1170 °C, while in the model system it is formed at 1350 °C. A further increase of the liquid phase is similar for equilibrium and non-equilibrium processes. The formation of 100% melt in the model system occurs at temperature of 1640 °C. however, accounting for the real chemical composition, ash will be completely fused at temperature of 1590 °C.

The analysis of the formation of shale combustion products based on the actual chemical composition (Table 3) shows that a relatively small amount of the primary melt is formed at temperature of 1170 °C and comes to 6,4%.

Table 3. The melt amount produced by shale combustion product melting depending on eutectics melting

| System | Composition, (wt. %) | Temperature, (°C) | Eutectic melt, (%) | Total melt amount, (%) |
|---|--|----------------------|-----------------------|---------------------------|
| CaO-Al ₂ O ₃ -SiO ₂ | SiO ₂ – 60 Al ₂ O ₃ – 15 CaO – 25 | 1170 | 6.4 | 6.4 |
| FeO-SiO ₂ | SiO ₂ – 38 FeO – 62 | 1178 | 10.92 | 17.32 |
| MgO-Al ₂ O ₃ -SiO ₂ | MgO – 21 Al ₂ O ₃ – 22 SiO ₂ – 47 | 1355 | 5.44 | 22.76 |
| CaO-MgO-SiO ₂ | SiO ₂ – 43,6 MgO – 9,2 CaO – 47,2 | 1400 | – | – |
| CaO-SiO ₂ | SiO ₂ – 63 CaO – 37 | 1436 | – | – |
| Melting due to dissolution Al ₂ O ₃ и SiO ₂ | | 1500 | | 43 |
| MgO-SiO ₂ | SiO ₂ – 65 MgO – 35 | 1543 | – | – |
| Melting due to dissolution Al ₂ O ₃ и SiO ₂ | | 1550 | | 62 |
| Complete melting | | 1600 | – | 100 |

Melting of the next eutectic comprising 38% SiO₂ and 62% FeO, occurs at 1178°C with the formation of 10.92% of the eutectic melt. Further, the melt formation occurs due to MgO and SiO₂ bond at temperature of 1355 °C. The total melt amount is 22,76%. At further temperature increase, the melt is formed not due to eutectics melting, but rather dissolving silica and alumina oxides, and at 1600 °C the shale combustion product will be completely melted.

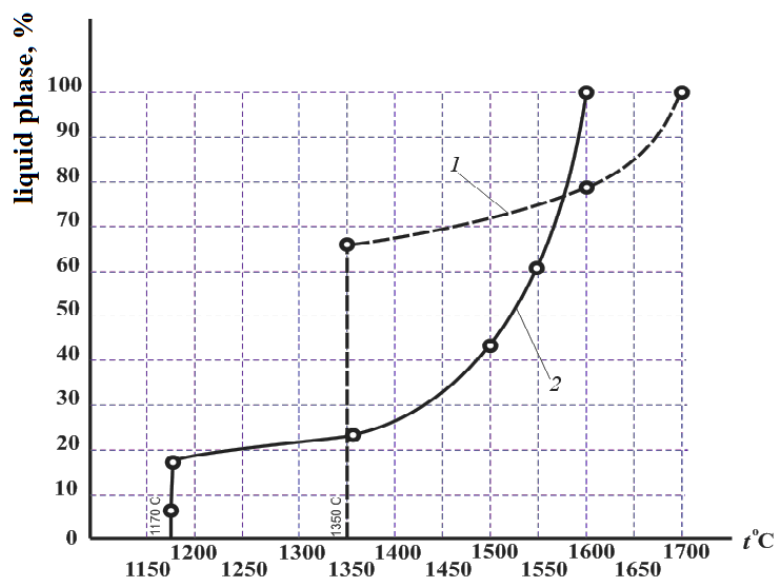


Figure 3. Shale combustion products fusibility curves:
1 - equilibrium dependence in CaO-Al₂O₃-SiO₂ system;
2 – non-equilibrium dependence of actual chemical composition

The analysis of fusibility curves (Fig. 3) shows that the starting temperature for the melt formation of shale combustion product does not exceed 1350 °C. At that, 6.4% of primary melt in the real system is formed at 1170 °C, and in the model system 66% of melt is formed at 1350 °C. The formation of 100% shale combustion product in the model system occurs at temperature of 1700 °C, but accounting for the real chemical composition, the shale combustion product is completely melted at temperature of 1600 °C.

4. Conclusions

Thus, it was found that the melting process of raw materials accounting for their real chemical composition is characterized by 50 °C decrease in the melting temperature in case of ash, and for shale combustion products it is characterized by the decrease of 100 °C. At that, the temperature of the primary melt produced by ash fusibility is formed in the real system at 1170 °C that is 180 °C lower than that in the model system. For shale combustion products, 6.4% of primary melt is formed in the real system at 1170 °C, while in the model system 59.6% of primary melt is formed at 1350 °C.

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