Investigation of the Rheological Properties of Complex Zeolite-Alumina Mixtures

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Abstract. In this present work, zeolite-alumina powder mixtures were prepared via mechanical activation technique using planetary ball milling. A comprehensive investigation of microstructure for the raw materials and the produced mixtures was done using different characterization techniques like XRD and SEM, furthermore the rheological behaviours of the mixtures has been accurately examined based on compaction pressure and time, as a result, the complex rheological properties and models of the prepared powder mixtures were described and estimated. The rheological behaviours show a substantial change with increasing the applied pressure.

Keywords: Zeolite-alumina mixtures, Rheological properties

1. Introduction

Recently, the technology and research in the ceramics industries are largely grown [1-34]. Ceramic technologies nowadays aim to produce superior ceramic products from relatively inexpensive raw materials to fulfil the optimum cost-benefit relationship. One of the popular techniques to achieve this goal is through the preparation of ceramic composites materials which normally show excellent properties and better performance, but the preparation of these materials demand adequate control of the processing steps. Because of the complexity of the ceramics structure and the diversities in the physical and mechanical properties, many shaping techniques could be used to form ceramics composite materials, for instance, mechanical compaction, extrusion, injection molding, casting, hydrothermal, sol-gel and various other forming methods [35]. Selecting an appropriate forming method is highly related to the rheological behaviours of the raw materials [36]. Among these forming techniques, powder compaction is an important method due to the high efficiency which enables this method to produce a large number of ceramics products in a comparatively short time. A high number of powders are used in the ceramic manufacturing, including ceramic powders for traditional ceramics such as kaolin, silica, feldspar, talc, etc. and ceramics powders for advanced ceramics like alumina, zirconia, zeolite, borides, carbides, nitrides, titanates, etc. These powders show different physical and chemical behaviours, which should be precisely manipulated to produce ceramic products with the required properties in a reproducible way [37]. Thus powder preparation for mechanical compaction is a fundamental step in the forming method, normally the size, the shape, the surface area and the purity of the powders have a strong connection to the rheology of the mixtures.
In this research work, zeolite-based alumina powder mixtures were produced via mechanical activation process. Investigation of the complex structure and microstructure of the mixture has been examined using different characterization techniques including X-ray diffraction (XRD) and scanning electron microscopy (SEM), moreover, the complex rheological characteristic of the mixture during the compaction has been described.

2. Experimental methods
Natural zeolite powders from Tokaj area (Hungary) and Al\_2O\_3 powder (98 %; MOTIM) were used as starting materials without further purification. Mixtures of these raw materials were produced using a mechanical activation technique. Appropriate amounts of these powders were measured based on the compositions shown in Table 1, the prepared mixtures were milled using a Retsch PM 400 planetary ball miller working at speed of 150 rpm for 15 minutes. The ground powders were pressed used hydraulic pressing machine, after that the applied force, the compaction time and the surface areas were determined.

| Zeolite % | Alumina % |
|-----------|------------|
| 100       | 0          |
| 90        | 10         |
| 80        | 20         |
| 70        | 30         |
| 60        | 40         |
| 50        | 50         |

3. Results and discussion
3.1 XRD investigations
Natural zeolite powder taken from Tokaj area (Hungary) contains many minerals like cristobalite, quartz, montmorillonite, calcite and clinoptilolite, which confirmed by XRD analysis, Figure 1 compares the XRD of the zeolite before and after milling, the difference in the intensity between the two graphs is due to the difference in the shape and size of the particles of zeolite before and after mechanical milling. Table 2 demonstrates the percentage of the Mineralogical constituents, Chemical composition and loss on ignition (LOI) of the natural zeolite in wt% obtained from XRD test. The highest amount of the mineral in zeolite was found to be silica in form of cristobalite which accounts to 50% and then montmorillonite with 30% then come the other minerals which represent 20% of the total amount.

Based on the composition of the oxide the overall amount of silica is found to be 82.92 wt% and the reminders are other oxides like alumina, magnesia and sodium oxide.

![Figure 1. XRD graph of the natural Zeolite](image-url)
Table 2 Chemical and mineralogical percentages of the natural zeolite (Tokaj, Hungary) obtained from XRD measurement

|        | Quartz | Cristobalite | Montmorillonite | Calcite | Clinoptilolite | Total  |
|--------|--------|--------------|-----------------|--------|----------------|--------|
| wt %   | 8.00   | 50.00        | 30.00           | 2.00   | 10.00          | 100.00 |
| CaO    | 1.12   |              | 1.12            |        | 1.12           |        |
| SiO₂   | 8.00   | 50.00        | 19.13           | 5.79   | 82.92          |        |
| Al₂O₃  | 4.06   | 1.89         | 5.95            |        |                |        |
| MgO    | 3.21   |              | 3.21            |        |                |        |
| Na₂O   | 0.74   | 0.57         | 1.31            |        |                |        |
| CO₂    |        | 0.88         |                 | 0.88   | 0.88           | 0.88   |
| H₂O    | 2.87   | 1.60         | 4.47            |        |                |        |
| LOI    | 0.00   | 0.00         | 2.87            | 0.88   | 1.75           | 5.50   |

3.2. SEM examination of the starting raw materials.

The SEM investigation of the natural zeolite and alumina powders show the microstructure in Figure 2, the particle size of zeolite is estimated to be from 0.5 up to 25 µm while the particle size of alumina is in the range of 0.5-50 µm.

Figure 2. SEM images of a) natural zeolite and b) alumina powders

Figure 3 shows the microstructure of the zeolite-alumina mixtures after mechanical activation which shows a high size reduction of the particle size of the mixtures.

Figure 3. SEM images of the alumina- zeolite mixture powders a) 80 % zeolite-20 % alumina b) 70 % zeolite -30 % alumina milled in planetary ball milling
3.3 Rheological characteristics of the ceramic mixtures

Figure 4. b exhibit the co-relationship between the time and the applied pressure, the first part of the time represents the compaction time when the external pressure is applied and the second part illustrates the relaxation time when the applied pressure is released. The relaxation time takes long but never reached zero showing the residual strain. The relationship between the time and the deformation is shown in Figure 4. c the deformation decreased after removal of the applied pressure and kept constant for a long time. Figure 4 d shows the connection between the applied pressure and deformation. 100% zeolite exhibit the largest deformation due to the presence of a high number of pores in the structure which give a possibility for larger deformation under applied pressure.

![Figure 4.](image)

The compression chart with the estimated rheological behaviour and determined bulk modulus of the powder inside the forming die is shown in Figure 5 which done based in Gömze model [38-39] which applied to many studies [40-44], in the first stage and at the starting of the compression process when very low pressure is applied, a significant increase in deformation is obtained, this is because the particles are far away from each other, the mixture can be represented as viscous material which can be represented by Newton’s model, with increasing the applied pressure in the second stage the particles are getting closer to each other rearranging the structure by sliding over each other in this stage the materials can be illustrated as “quasi-plastic” material. Further stress in the third stage generates very small compaction in correspondence to high applied pressure, as the materials are highly densified and the particles of the mixture are very close to each other the relationship is non-linear, the materials can be treated as a viscous-elastic body. In the fourth stage, the materials are
highly densified a very low deformation is obtained corresponding to high applied pressure, friction occurs between the die and the particles of the material, the materials can be considered as the parallel-linked viscous-elastic body. In the last stage, the fracture is approaching and the particles are getting closer to each other, this results in high increase in pressure and very slow change in deformation in this stage, the materials can be modelled as “quasi-plastic” material. The bulk modulus of the materials inside the die is highly increased as the applied pressure is increased.

![Figure 5](image.png)

**Figure 5.** The compression chart with the determined rheological behaviour and bulk modulus of the powder inside the forming die

4. Conclusion

Zeolite-alumina powder mixtures were prepared via mechanical activation method using planetary ball milling. An exhaustive analysis of the rheological behaviours has been attentively investigated based on the compacting pressure and time, as a result, the intricate rheological characteristics and the expected model of the prepared powder mixtures were described and estimated. A strong connection has been found between the microstructure and rheological properties. The alumina-zeolite mixtures which have complex structure due to the existence of many minerals, for instance, alumina, quartz, cristobalite, montmorillonite, calcite and clinoptilolite. This complex structure reveals different rheological characteristic at different applied pressure. The mechanical stress relaxation takes place during the uniaxial pressing of ceramic mixtures and continue for a long time but never reach zero showing the residual strain.

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