Preparation of Glass-ceramics from Phosphogypsum

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Abstract: CaO-Al2O3-SiO2 glass-ceramics was prepared from phosphogypsum and studied by
differential thermal analysis (DTA) and X-ray diffraction (XRD). CaSO4 in phosphogypsum
decomposed into CaS and then it reacted with CaSO4 forming CaO and SO2 when the most
energy-efficient reaction by Factsage calculated. SiO2, AlPO4, CaSiO3 (wollastonite-1A) and
CaSiO3 (calcium silicate) were identified as the main phases in the glass-ceramics prepared
from phosphogypsum.

1. Introduction
Phosphogypsum is an industrial solid waste of the phosphoric acid production. Its main component is
CaSO4·2H2O[1] but it also contains soluble phosphorus, fluorine, heavy metals, organics and
radionuclides[2,3]. Five tons of phosphogypsum is discharged per ton of the phosphoric acid produced.
More than 150 million tons of phosphogypsum is generated every year in the world. China is the
world's largest producer of phosphate fertilizers, and, as a result, the largest producer of
phosphogypsum[4] generating 50 million tons of phosphogypsum per year. Such large amounts
combined with their low utilization seriously affect sustainable development of phosphorus chemical
industry[5]. When utilizing phosphogypsum, engineers must considering the environmental impact of
the treatment of phosphogypsum as well as its economic benefits. Typically, phosphogypsum is either
stored or reused, both of which are waste of resources and are potential environmental hazards.
Phosphogypsum is often reused as building material[6-10], such bricks and boards, cement, cement
retarders and soil conditioners, but all these utilization methods have low added value.

Glass-ceramics is a polycrystalline material with fine crystalline microstructure formed during its
controlled crystallization[11,12]. It is used as a high-grade building decorative material. Performance of
such glass-ceramics is superior to glass and ceramics with the same composition. Glass-ceramics
prepared from phosphogypsum can solve the problem of accumulated phosphogypsum waste. The
specific technique involves phosphogypsum decomposition into CaO by coal in the inert atmosphere,
which helps to fully utilize Al-Si in phosphogypsum. Remaining P2O5 and F can act as nucleating
agents promoting the crystallization of glass-ceramics. Fabrication of glass-ceramics from phosphogypsum will help to resolve wastefulness of the phosphorus chemical industry as well as to achieve high economic benefits.

2. Experimental design and methodology
Phosphogypsum (from Yunnan Province in China) was ground, sieved with 180 mesh and dried at 105 °C for 24 h. Table 1 shows chemical composition of the phosphogypsum obtained using X-ray fluorescence (XRF). Its primarily compound is CaSO$_4$ (see Table 1 and Figure 1). Composition of lignite was determined by carbon-sulfur analyzer. Elemental and proximate analyses of lignite are given in Tables 2 and 3.

| Component | CaO | SiO$_2$ | Al$_2$O$_3$ | K$_2$O | P$_2$O$_5$ | F | Fe$_2$O$_3$ | Na$_2$O | SO$_3$ | Others |
|-----------|-----|---------|-------------|--------|-----------|---|-----------|--------|--------|--------|
| Content(wt%) | 29.82 | 9.43 | 0.24 | 0.09 | 2.04 | 0.64 | 0.13 | 0.04 | 40.86 | 16.72 |

Table 1 Composition of phosphogypsum obtained from a chemical factory in Yunnan Province

![XRD pattern of phosphogypsum](image)

Table 2 Elemental analysis of lignite from Yunnan Province

| Elemental analysis | C | H | O | N | S |
|-------------------|---|---|---|---|---|
| Content(wt%) | 62.47 | 4.36 | 30.73 | 1.35 | 1.09 |

Table 3 Proximate analysis of lignite from Yunnan Province

| Proximate analysis | Ash | Volatile matter | Moisture | Fixed carbon | Low heating value (kJ/kg) |
|--------------------|-----|-----------------|----------|--------------|--------------------------|
| Content(wt%) | 6.54 | 50.45 | 25.7 | 46.31 | 17820 |

To extract CaO, phosphogypsum and coal with a mass ratio of 10:1 were mixed and heated at 1200 °C. The resulting CaO was then mixed with SiO$_2$ and Al$_2$O$_3$ to obtain CaO-SiO$_2$-Al$_2$O$_3$ (CAS) glass-ceramics (see Table 4).

| Sample NO. | CaO | SiO$_2$ | Al$_2$O$_3$ | Amount |
|------------|-----|---------|-------------|--------|
| PG/L10    | 32  | 63      | 5           | 100    |

In order to prepare glass-ceramics, the powders were melted at 1400 °C for 2 h. The as-cast and treated samples of the parent glass were first annealed at 600 °C for 2 h, after which they were allowed to cool naturally to the room temperature in order to eliminate internal stresses. CAS glass samples were analyzed by differential thermal analyzer (TG/DTA, HCT-3) in N$_2$ atmosphere at 10 °C/min using alumina powder as a reference. 15 mg of each sample (reground after annealing and sieved through the 180 mesh) was used. Powder XRD patterns were recorded using X-ray diffractometer (D/max-2200) with Cu K$_\alpha$ radiation under applied acceleration voltage of 36 kV and current of 30 mA using in the 2θ 5-90° range with 3°/min step. Crystal phases were identified using Jade 5.0 software.
Bulk density was determined by the Archimedes method. Water absorption, acid and alkaline resistance were analyzed according to the building material industry standard JC/T 872-2000.

3. Results and discussion

3.1. Thermodynamics of phosphogypsum decomposition

The Gibbs free energy $\Delta G$ is an important parameter of the chemical reaction according to the thermodynamics theory. The reaction can be occurred when $\Delta G < 0$. The more negative $\Delta G$ value, the more likely the reaction proceeds. Calculation of the Gibbs free energy $\Delta G$ is very difficult if the reaction conditions are complex. Gibbs free energy of phosphogypsum decomposition was determined using Factsage software. Factsage can be used to calculate various reactions, thermodynamic properties, phase equilibrium in the field of chemical thermodynamics. Thermodynamics of phosphogypsum decomposition was performed using Factsage software. Phosphogypsum decomposition undergoes many different reactions\[^{13}\]. Since we were mostly interested in reaction of phosphogypsum with carbon, we chose the following chemical reactions:

$$2\text{CaSO}_4 \rightarrow 2\text{CaO} + 2\text{SO}_2(g) + \text{O}_2(g) \quad (1)$$

$$2\text{CaSO}_4 + \text{C} \rightarrow 2\text{CaO} + 2\text{SO}_2(g) + \text{CO}_2(g) \quad (2)$$

$$\text{CaSO}_4 + 4\text{C} \rightarrow \text{CaS} + 4\text{CO}(g) \quad (3)$$

$$3\text{CaSO}_4 + \text{CaS} \rightarrow 4\text{CaO} + 4\text{SO}_2(g) \quad (4)$$

Three of these reactions produce CaO and SO$_2$: reaction 1 is direct decomposition of CaSO$_4$ into CaO and SO$_2$; CaSO$_4$ decomposes into CaO and SO$_2$ with the presence of C in reaction 2; CaSO$_4$ decomposes first into CaS in reaction 3 and then reacts with CaSO$_4$ forming CaO and SO$_2$ according to the reaction 4. Thermodynamic data for all these reactions are shown in Table 5.

| Temperature (°C) | $\Delta G_{\text{Reaction 1}}$ (kJ/mol) | $\Delta G_{\text{Reaction 2}}$ (kJ/mol) | $\Delta G_{\text{Reaction 3}}$ (kJ/mol) | $\Delta G_{\text{Reaction 4}}$ (kJ/mol) |
|------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| 100              | 801.26                                 | 406.68                                 | 252.53                                 | 774.29                                 |
| 300              | 689.96                                 | 350.49                                 | 108.31                                 | 623.34                                 |
| 500              | 580.89                                 | 185.38                                 | -34.39                                 | 475.73                                 |
| 700              | 474.05                                 | 78.23                                  | -175.00                                | 331.44                                 |
| 900              | 369.50                                 | -26.54                                 | -313.54                                | 190.57                                 |
| 1100             | 267.28                                 | -128.91                                | -450.08                                | 53.25                                  |
| 1200             | 217.05                                 | -179.19                                | -517.63                                | -14.06                                 |
| 1500             | 72.47                                  | -323.84                                | -716.24                                | -206.76                                |
| 1700             | -16.91                                 |                                       |                                       |                                       |

If phosphogypsum decomposition proceeds through reaction 1, then, according to the thermodynamic data in Table 5, phosphogypsum decomposition temperature will be ~ 1700 °C. Gibbs free energy of this reaction will be ~ -16.91 kJ/mol. Analysis of the thermodynamic data showed that it is very difficult to decompose phosphogypsum into CaO and SO$_2$. Gibbs free energy of reaction 2 is $\Delta G = -26.54$ kJ/mol at 900 °C. This reaction requires much less energy comparing with the self-decomposition reaction 1. Reaction 3 can occur at 500 °C as its Gibbs energy at this temperature is calculated as $\Delta G = -34.39$ kJ/mol. In this work, decomposition reaction of calcium sulfate was carried...
out according to the reactions 3 and 4 with some adjustment to the experimental conditions.

3.2. Differential thermal analysis and phase analysis

Peak temperature of crystallization \( (T_p) \) of phosphogypsum determined from the DTA was 943.5 °C (see Figure 2). At this temperature, material transforms from its glassy short-range ordered amorphous state to the long-range ordered crystalline state.

![Figure 2 DTA curves of CAS glass-ceramics](image)

Thus, after a 2 h homogenization step at 780°C, the samples were heated at 943.5°C for 1.5 h to obtain microcrystalline glass-ceramics. Then the samples were ground in an agate mortar and analyzed by XRD.

![Figure 3 XRD patterns of CAS glass-ceramics](image)

The main components of the glass-ceramics were quartz (\( \text{SiO}_2 \) PDF:46-1045), cristobalite (\( \text{SiO}_2 \) PDF:39-1425), aluminum phosphate (\( \text{AlPO}_4 \) PDF:11-0500), wollastonite-1A (\( \text{CaSiO}_3 \) PDF:42-0547) and calcium silicate (\( \text{CaSiO}_3 \) PDF:01-0720) (see Figure 3).

3.3. Morphology and material properties

The photograph of the sample is shown in Figure 4. No transparent glass body can be seen. The color of glass-ceramics in the sample is shown in white, which shows excellent nucleation and crystallization.

![Figure 4 The photo of glass-ceramics sample prepared from phosphogypsum](image)

Density refers to the mass of mineral unit volume which mainly reflects the chemical composition and crystal structure of minerals. It is light grade when the relative density is less than 2.5 according to
the classification of mineral relative density. Therefore, the glass-ceramics prepared from phosphogypsum belong to light grade mineral (see Table 6). The lower the value of acid resistance, the better the acid resistance of the sample is. The lower the water absorption rate and the smaller the porosity, the denser the grain size is. The lower the alkali resistance value, the better the alkali resistance of the sample is. Thus, glass-ceramics prepared in our work from phosphogypsum is superior to marble in hardness, acid resistance, water absorption and alkali resistance.

### Table 6 Properties of the glass-ceramics prepared from phosphogypsum

| Properties       | Glass-ceramics | Marble     |
|------------------|----------------|------------|
| Density (g/cm³)  | 2.3            | 2.5~2.7    |
| Acid resistance  | <1             | 10.3       |
| Water absorption | <0.1           | 0.5~0.3    |
| Alkali resistance| <0.5           | 0.6        |

4. Conclusions

(1) This study provides the theoretical basis for the most energy-efficient use of phosphogypsum: CaSO₄ in phosphogypsum is first converted to CaS by reaction with C in the reduction atmosphere, and then CaS and CaSO₄ react to CaO and SO₂.

(2) Glass-ceramics produced from phosphogypsum consisted of quartz, cristobalite, aluminum phosphate, wollastonite-1A and calcium silicate (CaSiO₃) were showed in this experiment. The color this glass-ceramics was white and its properties were found to be superior to marble in hardness, acid resistance, water absorption, and alkali resistance. These properties make glass-ceramics fabricated from phosphogypsum a promising decorative building material.

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Reference

[1] Ma L P, Ning P, Zheng S, Du Y L. (2010) Reaction mechanism and kinetic analysis of the decomposition of phosphogypsum via a solid-state reaction. Ind. Eng. Chem. Res., 49: 3597-3602.

[2] Wang X L, Zhang Z Y, Yang X S, Zhong B H. (2011) Analysis on new approaches for utilization of phosphogypsum in China. Mod. Chem. Ind., 31: 1-3.

[3] Al-Masri M S, Amin Y, Ibrahim S, Al-Bich F. (2004) Distribution of some trace metals in Syrian phosphogypsum. Appl. Geochem., 19: 747-753.

[4] Yang X S, Zhang Z Y, Wang X L, Yang L, Zhong B H, Liu J F. (2013) Thermodynamic study of phosphogypsum decomposition by sulfur. J. Chem. Thermodyn., 57: 39-45.

[5] Ma L P, Du Y L, Niu X K, Zheng S Z, Zhang W. (2012) Thermal and kinetic analysis of the process of thermochemical decomposition of phosphogypsum with CO and additives. Ind. Eng. Chem. Res., 51: 6680-6685.

[6] Singh M. (2002) Treating waste phosphogypsum for cement and plaster manufacture. Cement. Concrete. Res., 32: 1033-1038.

[7] Reijnders L. (2007) Cleaner phosphogypsum, coal combustion ashes and waste incineration ashes for application in building materials: A review. Build. Environ., 42: 1036-1042.
[8] Zhou J, Gao H, Shu Z, Wang Y X, Yan C J. (2012) Utilization of waste phosphogypsum to prepare non-fired bricks by a novel Hydration–Recrystallization process. Constr. Build. Mater., 34: 114-119.

[9] Shen W G, Gan G J, Dong R, Chen H, Tan Y, Zhou M K. (2012) Utilization of solidified phosphogypsum as Portland cement retarder. J. Mater. Cycles. Waste., 14: 228-233.

[10] Lima M, Braz L, Veiga J. (2013) Effect of phosphogypsum on the clinkerization temperature of Portland cement clinker. Mater. Sci. Forum., 732: 94-99.

[11] Yang Z H, Lin Q, Lu S C, Yong H. (2014) Effect of CaO/\text{SiO}_2\text{ ratio on the preparation and crystallization of glass-ceramics from copper slag. Ceram. Int.}, 40: 7297-7305.

[12] Cao J, Wang Z. (2013) Effect of Na_2O and heat-treatment on crystallization of glass-ceramics from phosphorus slag. J. Alloy. Compd., 557: 190-195.

[13] Zheng S C, Ning P, Wang F, Cheng F X, Hu F E. (2013) Study on preparation of sulfur dioxide and lime by thermal decomposition of phosphogypsum. Inorg. Chem. Ind., 45: 45-47.