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Synthesis of lead sulfide by heavy metal gypsum matched with lead paste

De'an Pan [a], Shuhuai Jia [b], Lijie Qiao [b], Tingting Liu [a], Yufeng Wu [a, *], Alex A. Volinsky [c]

[a] *Institute of Circular Economy, Beijing University of Technology, Beijing 100124, PR China*
[b] *Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, PR China*
[c] *Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA*

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ABSTRACT

The heavy metal gypsum is a hazardous solid waste, which is from the process of lead and zinc metallurgical industry. In this method, heavy metal gypsum and lead paste were used to synthesize PbS by pyrogenic attack. First synthesize CaS by the reducing of heavy metal gypsum that the pulverized coal was used as a reduction agent. Then the production CaS reacted with lead paste to synthesize PbS and the product CaO. The production PbS can be reused as raw materials for the process of lead metallurgical industry and CaO can be used to replace some slag forming constituents or smelting flux. The two-steps method reaction temperatures were 1173 K and 1073 K respectively in a protective atmosphere of nitrogen, wherein the second step was the rate-controlling step. In the final product, the percentage of lead was 70.89%, which exceeded the standard level of lead of industry standard for the nonferrous industry of China. At last, lead element was almost removed from waste gypsum as PbS, with some lead free about 4.5% which can be recycled in the dust catcher system. In this way, heavy metal gypsum can be recycled environmentally, economically and sustainably.

1. Introduction

Heavy metal gypsum derives from the production process of lead and zinc of the metallurgical industry. With the consumption of flue gas by double-absorption processes, a lot of strong-acid waste water called waste acid was produced as the by-product (Daun et al., 2010; Shang et al., 2010); . There are a number of harmful elements concluded in the waste acid such as heavy metals Pb, Zn, Hg, As, Cd et al. Heavy metal gypsum is the product of the treatment of waste acid with processes such as the neutralization precipitation method and the sulfide-neutralization method et al. (Shao and Yang, 2011; Ma, 2011). Therefore, the main component of heavy metal gypsum is gypsum with some heavy metals Pb, Zn, Hg, As, Cd et al. Since a small amount of heavy metal oxides and hydroxides, especially the leaching toxicity of Cd exceeding the Environmental Protection Agency standard, heavy metal gypsum is deemed as a hazardous solid waste.

Due to the strong liquidity and solubility of heavy metals in the solid waste, heavy metals are easy to permeate into the water and soils surroundings, which will lead to accumulate in water, plants and animals, eventually accumulate in human bodies (Pelfrene et al., 2012). While these heavy metal ions are harmful to human health even a little. Consequently, the heavy metal gypsum is harmful to the environment and human (Briki et al., 2015). In the Qingshuitang industrial district of the southern city of Zhuzhou in China, over 200,000 tons of heavy metal gypsum are produced annually, with the toxic elements concentration in the farmlands near the factories exceeding the standards, and the core 15 km^2 are seriously polluted (Zhu, 2012). Since such vast amount of heavy metal gypsum piles up and couldn't be recycled effectively, the heavy metal gypsum is limiting the sustainable development of lead and zinc metallurgical industry. As the exits of heavy metals, the heavy metal gypsum can't be recycled in the construction industry and agriculture. While there are abundant calcium and sulfur contained in the heavy metal gypsum, which is up to 80 wt% that is a very good renewable resource for sulfur and calcium resources. So, it is necessary to develop an economical and environmental technology for the management and utilization of heavy metal gypsum. Since the studies of utilization of heavy metal gypsum is less, and the heavy metal gypsum is one of the waste gypsum, the study of the circulation utilization of heavy

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* Corresponding author.
E-mail address: wuyufeng3r@126.com (Y. Wu).

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metal gypsum can refer to the investigation of recycling of waste gypsum.

The main component of waste gypsum is $CaSO_4$. The same with heavy metal gypsum, the discharge amount of waste gypsum is also enormous. Every year, there are more than 20 million tons' waste gypsum yielded. Now the main treatment method of waste gypsum is pile-up. There are some reuses of waste gypsum, using as construction materials such as making plasterboard and bricks, agricultural conditioner, and other fields to recycle as fertilizer, and filler materials of roads. As the study of Manjit Singh and Mridul Garg, waste gypsum was used to make of anhydrite cement. When the heating temperature up to 1000 °C, a stable anhydrite was produced. And with the sodium sulfate and ferrous sulfate activators, the strength of anhydrite cement would achieve maximum attainment (Singh and Garg, 2000). Chea Chandara et al. use waste gypsum to substitute the natural gypsum to produce Portland cement, because waste gypsum contains more hemihydrate up to 12.45%, however, natural gypsum is 1.61%. The result showed that cement waste gypsum set faster than cement natural gypsum, at average of 15.29% and 13.67%. So, the waste gypsum can be used as an alternative material to natural gypsum to produce Portland cement (Chandara et al., 2009). At the same time, the abundant resource of calcium and sulfur elements in the waste gypsum, so new methods are more meaningful to recycle waste gypsum as high added-value products for calcium and sulfur resources.

The method for recycling of resource calcium and sulfur from waste gypsum is mainly the reduced decomposition of waste gypsum to get the productions such as CaS, CaO, SO_2, further to get the chemical products sulfur acid, thiourea, sulfur, calcium carbonate et al. For example, Nengovhela and Strydom et al., use activated carbon to reduce gypsum as CaS. Then the reaction of gaseous CO_2 with CaS slurry generate H_2S gas and $CaCO_3$ precipitation. And H_2S was used to generated element sulfur by PIPco process (Nengovhela et al., 2007). While Doucet, and Beer et al., gain CaS with thermally reducing the waste into calcium sulfide similarly, then use an indirect aqueous CaS carbonation process to generate high-grade precipitated $CaCO_3$ in which H_2S was used to improve aqueous dissolution of CaS. In this method waste gypsum was recycled as Calcite and element sulfur (Doucet et al., 2015). As for the decomposition of waste gypsum, scholars have been making efforts to research the mechanism of the reduction decomposition of waste gypsum. The decomposition of waste gypsum contains two stages, one is the reduction of waste gypsum that CaS is the intermediate production, and the other is the oxidation stage wherein the intermediate product CaS reacts with $CaSO_4$ to convert into CaO and SO_2. As the research of Vander Merwe and Strydom et al. the reaction of carbon and waste gypsum produced CaS and CaO. However, the formation of CaS and CaO depended on the heating rate and catalysts. In brief, the reaction between and carbon and $CaSO_4$. was complex and competitive Merwe et al., 1999). Da Zheng et al., researched that the reduction decomposition of FGD gypsum with anthracite was a two-step reaction, the CaS was intermediate in the conversion of $CaSO_4$- CaO (Zheng et al., 2013).

The reduction decomposition of waste gypsum most occurs with many reduction agents and in different atmospheres. The decomposition temperature of the waste gypsum is about 1673 K, while the decomposition temperature declines obviously with reducing agents. For instance, the decomposition temperature has been decreased to 1273 K with high-sulfur-concentration coal studied by Shaocong Zheng et al.

Some researchers pay attention on different reducing gases such as CO, H_2S, H_2, and CS_2. As the research result of Hongjian and Qingjie, hydrogen and carbon monoxide were used as reducing agent to react with $CaSO_4$ to generate oxygen carrier to realize an Chemical looping combustion with the influence of $CaCO_3$ nanoparticles (Tian et al., 2010). Further, Byung and Hong, use hydrogen to reduce $CaSO_4$ with nickel catalyst will be more effective. And more important, it discovered that the solids can be reusable for repeated cycles to avoid generating secondary pollutants. It provides an important research content Hong and Kim, 2002). Other researchers study the reduction with CO or CO-CO_2-N_2. As a result, at 1273 K, in a 2 vol% CO and 30 vol% CO_2 atmospheres, the decomposition for CaSO4 to CaS get an apparent conversion value of 0.91 (Okumura et al., 2003). While Oh J. S., and Wheelock researched that $CaSO_4$ was treated with a mixture atmosphere of CO-CO_2-SO_2-N_2, at low potentials ($P_{CO}/P_{CO2} \leq 0.01$), $CaSO_4$ convert to CaO. And at moderate potentials ($P_{CO}/P_{CO2} \approx 0.02$), $CaSO_4$ rapidly convert to CaO, then converted to CaS more slowly (Oh and Wheelock, 2002).

For example, the waste gypsum may react with CO as follows.

$$CaSO_4 + CO = CaO + SO_2 + CO_2 \tag{1}$$

$$CaSO_4 + 4CO = CaS + 4CO_2 \tag{2}$$

$$CaSO_4 + CaS = CaO + 2SO_2 \tag{3}$$

Wherein equation (1) is the total reaction, the decomposition of waste gypsum is deemed to two stages that the reduction stage and the oxidation stage correspond with equation (2) and equation (3). However, when the decomposition occurs with reducing gases, the reactions and products vary according to the conditions and the concentration gases, which is difficult to control. Because the reducing reaction with reducing agents, a large excess of reducing gases is required to create an environment with no oxygen.

With different sulfur and carbon solid reducing agents such as sulfur, coke, coal, charcoal etc., some scholars conduct the reducing decomposition experiments of waste gypsum with solid reducing agents. A solid-state reaction was studied by reaction mechanism and kinetic analysis of the decomposition of phosphogypsum by Liping and Ping et al., high-sulfur-concentration coal was used as a solid reducer to react with phosphogypsum in a nitrogen atmosphere at different condition. The result showed that the forming of CaS depends on the heating rate and the size of coal. When the size was 60 mesh, the decomposition of $CaSO_4$ gets high recovery of CaO Ma et al., 2010). Also in the study of Shaocong Zheng and Ping Ning et al., high-sulfur concentration coal was used to reduce phosphogypsum in the protection of nitrogen atmosphere. When the temperature was about 1000 °C, and mole ratio of C: CaSO4 was 1.2:1, it is the optimum condition to produce SO_2, the maximum SO_2 concentration was 7.6%vol. In the process, the conversion to sulfur dioxide was 92.2%, and the desulfurization rate was 95.16% (Zheng et al., 2011). The same study was done by Beer and Maree, investigate that the carbonation of CaS to convert into $CaCO_3$. (Beer et al., 2014). Moreover, the reaction between sulfur and phosphgypsum was studied. A process with sulfur as reducer was proposed to decompose phosphgypsum. And it proved that the reaction was lower which is 250 K. The enthalpy of reaction enthalpy of reaction 27.95% less than coal reducing process (Yang et al., 2013). This method can improve an important reducing agent for the decomposition of waste gypsum. The reaction between waste gypsum and sulfur or carbon are as follows.

$$2CaSO_4 + S = 2CaO + 3SO_2 \tag{4}$$

$$CaSO_4 + 2S = CaS + 2SO_2 \tag{5}$$

$$3CaSO_4 + CaS = 4CaO + 4SO_2 \tag{6}$$

$$2CaSO_4 + C = 2CaO + CO_2 + 2SO_2 \tag{7}$$

$$CaSO_4 + 2C = CaS + 2CO_2 \tag{8}$$

$$CaS(s) + H_2O + CO_2(g) \rightarrow H_2S(g) + CaCO_3(s) \tag{9}$$

The production of CaS is an intermediate for reduction stage of $CaSO_4$ with sulfur and carbon. Then CaS can react with $CaSO_4$ to get CaO and SO_2. CaO can be used in the production process of cement building materials or as the SO_2 capture. At the same time, the intermediate product CaS can be used in the process of recovery of sulfur and calcium carbonate or to prepare sulfur acid and thiourea and so on. For example, some scholars use CaS as a reducing agent to react with aqueous solution of CO_2 to obtain H_2S to prepare sulfur acid and calcium carbonate. Changxin Li and Hong Zhong et al. utilize the intermediate product CaS to react with manganese oxide ores to extract manganese by reduction acid leaching from low-grade manganese oxide ores (Chang-Xin et al., 2015).

In this paper, heavy metal gypsum was reduced by pulverized coal to get CaS in a protective atmosphere of nitrogen. And the first-step production CaS and pulverized coal was attempted to use as reducing agents to react with lead paste to obtain PbS, which can be reused in the process of lead metallurgical industry. Meanwhile, the by-product CaO can be used as a slag forming constituent in the process of lead smelting. So the resources of calcium and sulfur in waste gypsum can be recycled sufficiently.

2. Experimental section

2.1. Materials preparation and characterization

Heavy metal gypsum used in the experiment was generated at a plant of lead and zinc metallurgy in Zhuzhou city of Hunan province of China. The heavy metal gypsum collected was dried by heating at 573 K for 60 min. Then heavy metal gypsum was crushed and sieved less than 1 mm. And the sample CaS that obtained by the reducing of heavy metal gypsum with the reducing agent pulverized coal, was saved in a sealed plastic package to avoid the spontaneous oxidation with moist air. Because the CaS is not stable very well. Furthermore, the lead paste sample is generated at a plant of battery manufacturing plant in a city of Zhejiang province of China.

The chemical compositions of the samples and products were analyzed by XRF (X-ray fluorescence spectrum analysis) which was performed on the PANaytical Axios X-ray fluorescence spectrometer (Netherlands), and the mineralogical composition of samples and products were analyzed by XRD (X-ray diffraction analysis) that was conducted on the Rigaku D/MAX-RB X-ray Diffractometer (Rigaku, Japan) using the Cu-Kα radiation at 40 kV and 150 mA, 0.02° per step, 10°/min. Furthermore, the accurate content of elements in samples and products were determined by the ICP-MS ((Inductively coupled plasma mass spectrometry) which was performed on Thermo Fisher Scientific ICAP 6300 instrument (United States).

The chemical compositions and the mineralogical compositions of raw materials were determined and presented respectively. The chemical compositions of the samples heavy metal gypsum and lead paste are given in Table 1 and Table 2. Table 1 shows that the main composition of heavy metal gypsum is $CaSO_4$, and Table 2 shows that the main compositions of lead paste are $PbSO_4$ and PbO. And the main composition of pulverized coal is carbon indicated as Table 3.

Table 1
Chemical compositions of heavy metal gypsum (wt.%).

Composition	CaO	SO_3	SiO_2	F	As_2O_3	Fe_2O_3	ZnO	PbO	CdO	HgO
Content	42.03	37.02	3.08	2.49	0.28	6.12	2.72	0.3	0.2	0.02

Table 2
Chemical compositions of lead paste (wt.%).

Composition	PbO	$PbSO_4$	SiO_2
Content	49.8	32.6	4.6

Table 3
Chemical composition of pulverized coal (wt.%).

Composition	water	volatiles	fixed carbon	ash content
Content	0.85	23.4	54.8	20.95

In addition, the XRD patterns of the samples heavy metal gypsum and lead paste are shown in Fig. 1 and Fig. 2. Just as the XRD patterns in Fig. 1 indicated that the heavy metal gypsum is mainly composed of $CaSO_4 \cdot 2H_2O$. In the experiments, heavy metal gypsum was dried at 573 K for 60 min to remove water of hydration. What's more, the main compositions of lead paste are $PbSO_4$ and PbO as Fig. 2 shows.

2.2. Experimental procedures

In this study, CaS and pulverized coal was attempted to use as reducing agents to react with lead paste in the synthesis of PbS which was aimed to recycle the resource of lead and sulfur elements, while the reducing agent of CaS was synthesized by the experiment that the reduced decomposition of heavy metal gypsum with the reducing agent pulverized coal. So the synthesis of PbS was designed into two steps to synthesize the intermediate product CaS and the final products PbS and CaO.

Before the experiments, some thermodynamics calculations were made to analyze the reaction temperature and types of production according to the main components of raw materials. At the same time, the possibility can be examined. In the thermodynamics calculation, HSC software was used as a tool to calculate the theoretic reaction temperature.

The first step was the reaction between heavy metal gypsum and pulverized coal to obtain CaS. Heavy metal gypsum and pulverized coal were mixed up uniformly, then the mixture was saved in a porcelain boat. And the porcelain was placed in the hot zone of a tube furnace. The tube furnace equipped with a programmable controller is presented as Fig. 3, which is also shows the experiment flows. The mixture was heated to 1173 K directly at a heating rate of 10 K/min, and kept for 120 min in the corresponding temperature, then cooled inside the furnace to room temperature in which nitrogen gases were used to provide a protective atmosphere throughout. Finally, the product was saved in sealed plastic package to avoid the spontaneous oxidation by moist air.

The second step was also conducted in the same tube furnace. The first-step product that was crushed and sieved less than 1 mm, lead paste and a little of pulverized coal were mixed up uniformly.

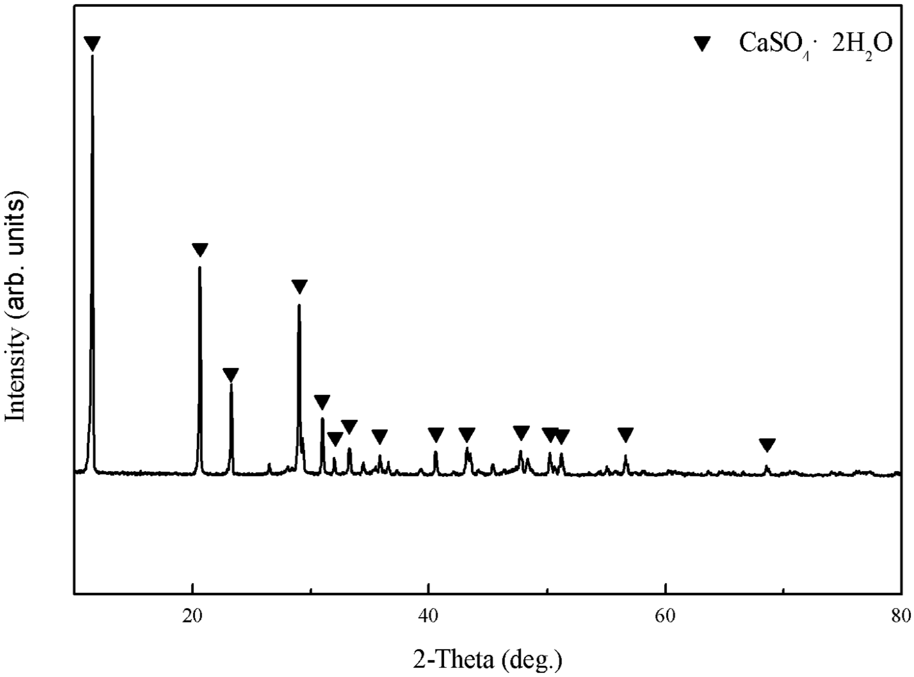

Fig. 1. XRD pattern of heavy metal gypsum.

Similarly, the mixture was placed in the hot zone of a tube furnace. In the second-step, the mixture was heated to 1073 K directly at a heating rate of 10 K/min, and kept for 60 min in the corresponding temperature, then cooled inside the furnace to room temperature in which nitrogen gases were also used to provide a protective atmosphere throughout. The obtained product collected in a plastic sample bag.

3. Result and discussion

3.1. The thermodynamic calculation of the reactions in the reaction between CaS and lead paste

In this paper, two steps were adopted to get the product CaS and react with lead paste. In the first step, the mixture which was

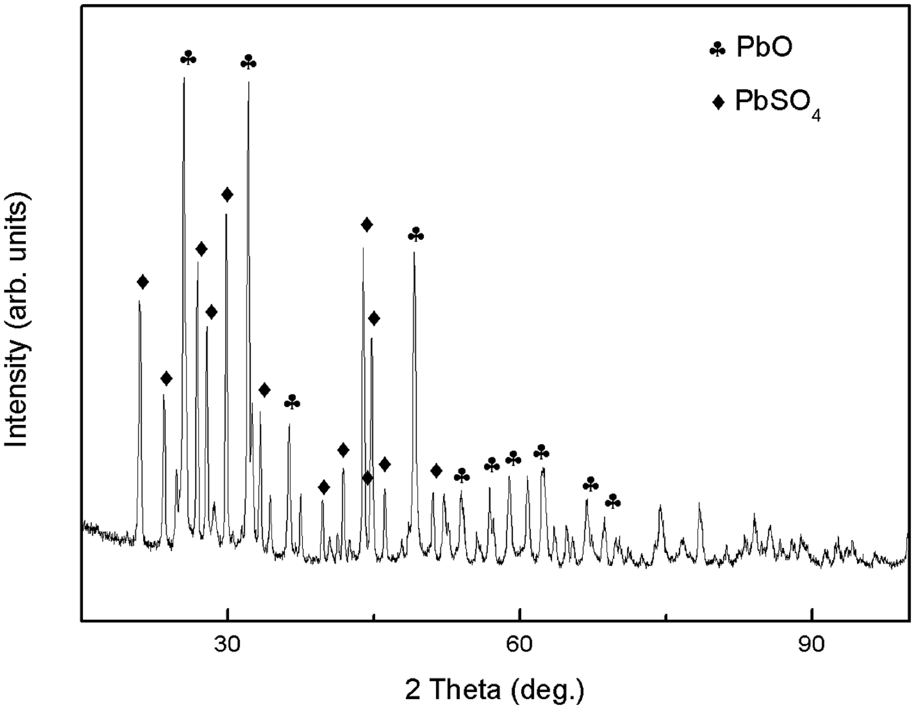

Fig. 2. XRD patterns of lead paste.

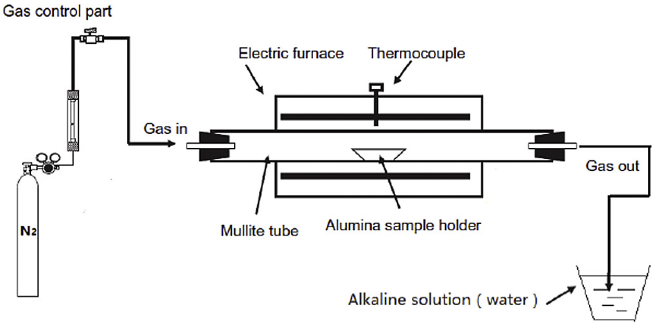

Fig. 3. The reaction vessel a tube furnace and experimental flow.

obtained by heavy metal gypsum mixed with pulverized coal, was heated in the tube furnace with the protection of nitrogen atmosphere. So the reaction in the first step was relatively uncomplicated. It is main the reaction between CaSO4 and carbon just as the chemical equation (10). And there are some process parameters to impact the condition for the reaction. As the study of Chen Honglai and Wang Zhigang et al., when the coal powder was exceed 25%, temperature was 870 °C, and reaction time was 2 h, the conversion rate of phosphygypsum through calculation was above 98%. In this paper, we also study the process parameters of reduction (Chen et al., 2011).

However, in the second step, the process was relatively complex. There were some reactions in the crucial step as follows. Liping Ma and Xuekui Niu used software and experiment to show that the CO and CO_2 useful to improving the decomposition effect and reduce the reaction temperature to 1100 °C. And when the coal particle size was 60 mesh–100 mesh, the heating rate was 5 °C/min, the CaS was about ten percent in solid product (Ma et al., 2011). In this paper we use a thermodynamics calculation to evaluation the change of Gibbs free energy for reactions. The results of thermodynamics calculation were shown as the change of Gibbs free energy with the increasing of temperature just as the Fig. 3.

$$CaSO_4 + 2C = CaS + 2CO(g) \tag{10}$$

$$3PbSO_4 + 4CaS = 4CaO + 3PbS + 4SO_2(g) \tag{11}$$

$$PbSO_4 + C = Pb + CO_2(g) + SO_2(g) \tag{12}$$

$$3PbSO_4 + 2CaS = 2CaO + 3Pb + 5SO_2(g) \tag{13}$$

$$CaS + PbO = CaO + PbS \tag{14}$$

$$PbSO_4 + 2C = PbS + 2CO_2(g) \tag{15}$$

$$2PbO + C = 2Pb + CO_2(g) \tag{16}$$

$$PbSO_4 + CaS = CaSO_4 + PbS \tag{17}$$

In the second step, main reaction equations are listed as equations (11)–(16). Fig. 4 presents the thermodynamic calculation results for the reactions in the two steps. Comparing equations (11) and (13), when $PbSO_4$ reacted with CaS, the main productions of lead such as PbS and element lead were obtained. However, as the Gibbs free energy curves, the absolute value of Gibbs free energy of the reaction (11) exceeded the value of the reaction (13). So the reaction (11) occurred easier than the reaction (13), when the temperature was below 1273 K. So the PbS was easier to get than element lead, when the $PbSO_4$ reacted with CaS. Similarly, comparing the reaction equations of (12) and (15), the absolute value of Gibbs free energy for reaction equation (15) was always larger than the reaction equation (12). It meant that the PbS was easier to obtain in the reaction between lead sulfate and pulverized coal. While the temperature was below 273 K, the reaction equations (14) and (16) both could occur spontaneously. According to the absolute value of Gibbs free energy, the reaction

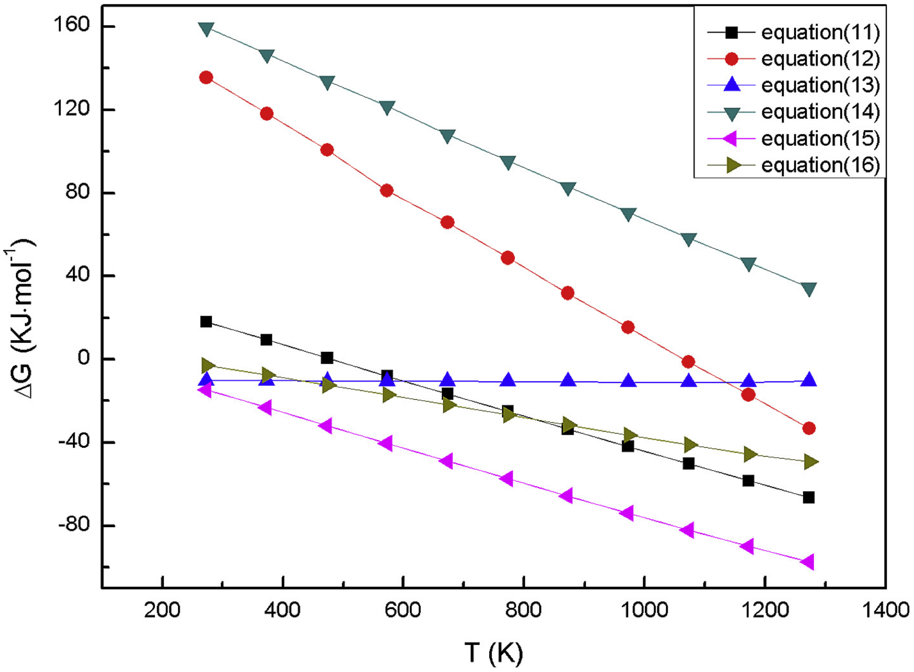

Fig. 4. Gibbs free energy curves of the reactions between waste gypsum and lead paste.

equation (16) was easier to occur. It meant metallic lead was easier to generate. But the actual production had to examine by actual experiments.

In brief, according to thermodynamic calculation, when lead paste in which the main chemical components are $PbSO_4$ and PbO reacted with CaS, the main production was PbS. And when the lead paste reacted with pulverized coal, the main production was PbS too. While when the lead paste and pulverized coal were mixed to heat, the product need to be examined by actual experiments. Meanwhile the appropriate react temperature and product had to be examined by actual experiments according to the result of thermodynamic calculation.

3.2. The study of the superior reaction temperature for reactions in the reaction between $CaSO_4$ and lead paste

According to the result of thermodynamic calculation, the reaction temperature and productions can be determined, but the actual temperature and productions have to be examined by the actual experiments between the main components of the lead paste and CaS and pulverized coal.

3.2.1. The reaction between $PbSO_4$ and CaS

According to the result of the thermodynamic calculation for the reactions between heavy metal gypsum and lead paste, the reaction between $PbSO_4$ and CaS occurred at the temperature of 873 K, and the production was PbS. Then the reaction was examined by the actual experiment between the agents of $PbSO_4$ and CaS.

The mixture of $PbSO_4$ and CaS were calcined at the temperatures of 873 K, 973 K and 1073 K. And the results of X-Ray powder diffraction were presented as Fig. 5. When the temperature was 873 K, the main phase components were $PbSO_4$, CaS and PbS. While the $PbSO_4$ and CaS were from the reactants. So CaS was the main product, but the quantity of PbS was relative low. And with the temperature increasing, the diffraction peak of PbS was becoming stronger. At the same time, the diffraction peaks of $CaSO_4$ were becoming stronger, the generation of which was just as equation (8). When the temperature increased to 1073 K, the phase components were only PbS and $CaSO_4$. As a result, the PbS and $CaSO_4$ were obtained in the reaction between $PbSO_4$ and CaS, wherein the $CaSO_4$ was really obtained as the by-product. Compared with the results from the thermodynamics calculation, the beginning reaction temperature of $PbSO_4$ and CaS was 873 K consistent, and when the temperature was 1073 K, the reaction gone to completion thoroughly. And to obtain the final product PbS, the reaction between $PbSO_4$ and CaS was the key reaction and the controlling reaction in the experiment to get PbS. So the reaction temperature for the temperature of the second step was better to choose at 1073 K.

3.2.2. The actual reaction between PbO and CaS

According to the thermodynamic calculation for the reactions between heavy metal gypsum and lead paste, the PbO would reacted with CaS, when the temperature was below 273 K and the metallic lead was easier to get. Then the actual experiments were conducted to examine the temperature and product.

Just as shown by the a) in Fig. 6, the XRD patterns of products which was obtained at 773 K, shows that the reaction between PbO and CaS not occurred. Because in the XRD patterns, the main phase components of products were PbO and CaS which were from the components of reactants. The diffraction peaks of PbS didn't appear in the product patterns, so the result shown that the reaction can't occur for the reasons of dynamic that the temperature can't achieve at the actual reaction temperature. And the b) in the Fig. 6, the XRD patterns that was for the products obtained at 873 K, shown the main phase components of the product are PbS and PbO which was from the reactant lead paste. The result was consistent with the conclusion of thermodynamic calculation. According to the XRD patterns, the diffraction peaks of CaS disappeared at 873 K which meant that the reaction gone to accomplish thoroughly. At 873 K, the reaction between PbO and CaS occurred, and the extent of reaction was

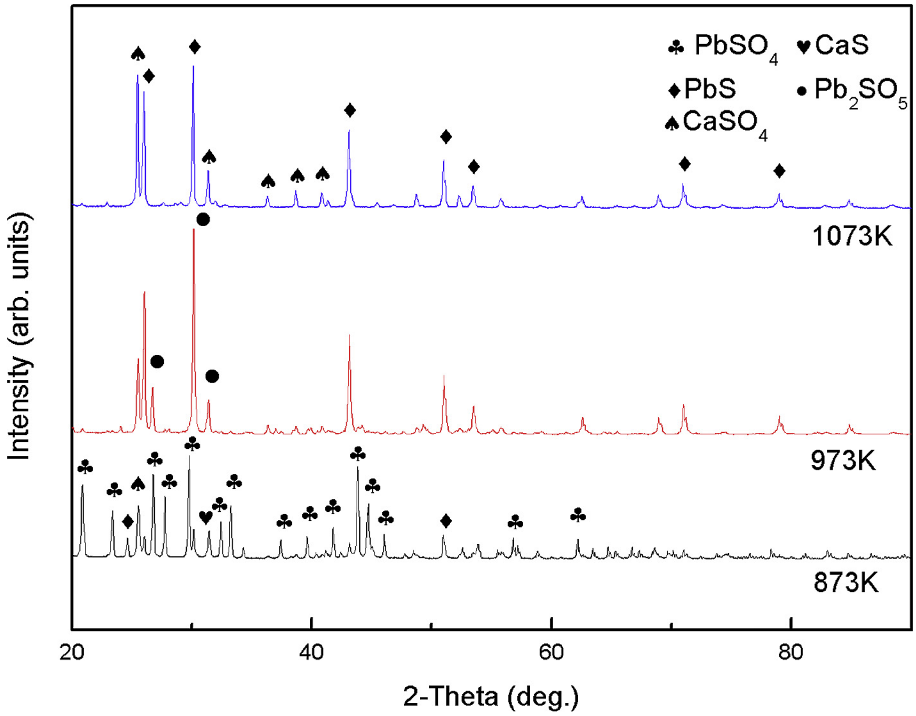

Fig. 5. XRD patterns of products obtained at different temperature of the reaction between $PbSO_4$ and CaS.

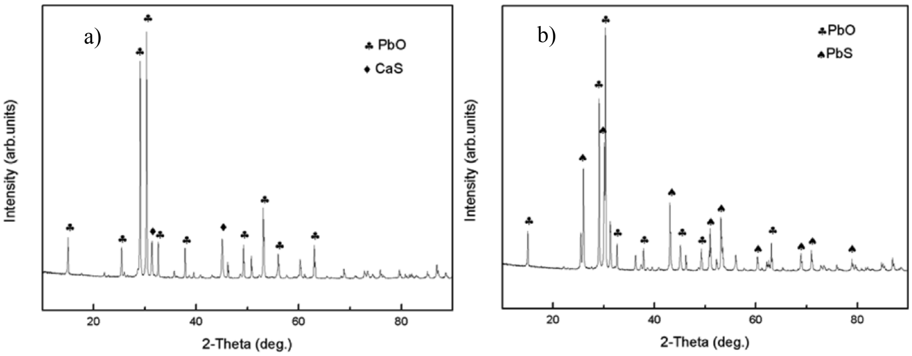

Fig. 6. The XRD patterns of productions of the reaction between PbO and CaS, a) was 773 K, b) was 873 K.

relatively thoroughly. The main products were PbS and CaO. In comparison with the result of thermodynamics calculation, the reaction temperature needed to be heated to 873 K to react thoroughly for some reasons on kinetics. So the appropriate reaction temperature of PbO and CaS was better to choose at 873 K or higher. Because the PbO was the main component in lead paste, the reaction of PbO and CaS was also one key reaction and controlled the reaction rate.

3.2.3. *The experiment of actual reaction between $PbSO_4$ and pulverized coal*

To examine the actual reaction temperature and products of the reaction between $PbSO_4$ and pulverized coal, and choose an appropriate reaction temperature, the experiments for the reaction were conducted. And the reactions were carried out at the temperatures of 973 K, 1073 K and 1173 K.

The products of the reaction between $PbSO_4$ and pulverized coal were composed of PbS, $PbSO_4$ and a small amount of metallic lead, indicated as the Fig. 7. When the reaction temperature was 973 K, the products were composed of PbS and $PbSO_4$. Therefore, at this temperature of 973 K, the $PbSO_4$ reacted with pulverized coal, and the reaction product was PbS. But $PbSO_4$ was still existed at this temperature, meaning that the reaction was not thorough. Then, as the increasing of temperature, the content of $PbSO_4$ was decreasing, just as Fig. 7 shows. When the temperature reached 1073 K, the phase components of products were PbS and a very small amount of metallic lead. What's more, when the temperature reached to 1173 K, the main phase components of products was same with the products at 1073 K without changing. However, the diffraction peaks of metallic lead become stronger. And the content of metallic lead in the product increases, which was not favor of the recycling of element lead because the metallic was easy to volatilize. For the phase components changed with the increasing of temperature, to obtain the objective product PbS as much as possible, it was better to choose the temperature 1073 K as the experiment temperature. The reaction between $PbSO_4$ and pulverized coal was considered because the pulverized coal was also chosen as the reducing agent to decrease the reducing temperature. In addition, the generation of $CaSO_4$ in the reaction between $PbSO_4$ and CaS needed to be prevented or removed. Compared with the theoretic calculation,

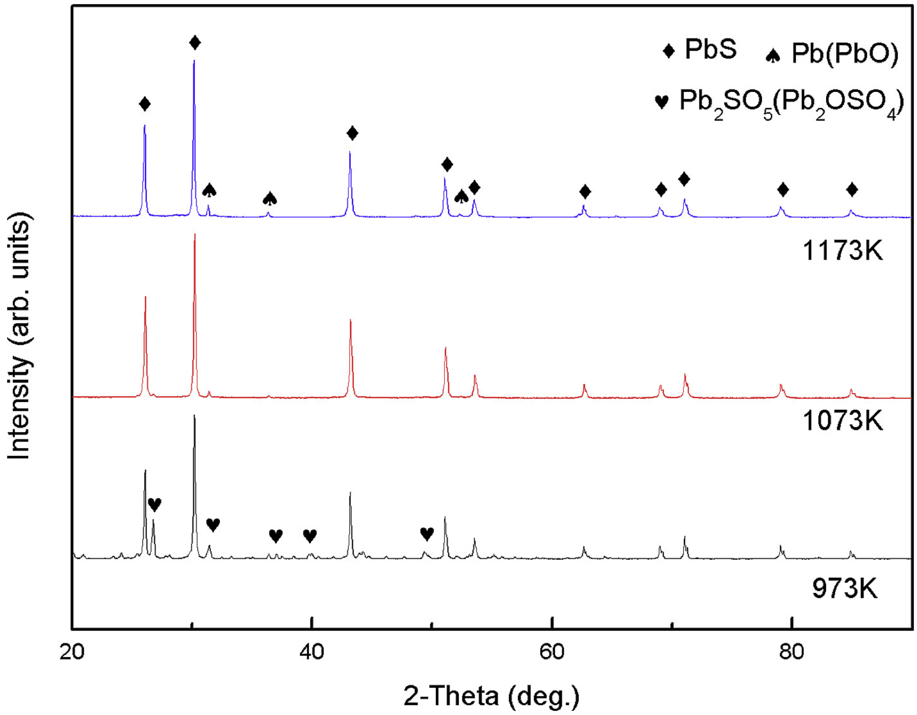

Fig. 7. XRD patterns of products from the reaction between $PbSO_4$ and pulverized coal at different temperatures.

the appropriate temperature was approximate the theoretical reaction temperature. Therefore, the experiment temperature for $PbSO_4$ and pulverized coal could be determined at 1073 K.

3.2.4. The reaction between PbO and pulverized coal

In this section, the reaction of PbO and pulverized coal occurred at 773 K, 873 K, 923 K and 973 K. Solid residuals were detected by the method of XRD. The XRD patterns of products at different temperatures were presented in Fig. 8.

Just as the a) in Fig. 8, the product from the reaction at 773 K, the main phase composition was PbO, C and metallic lead, wherein the peak of metallic was very weak. So the reaction that mainly occurred between PbO and C to obtain metallic lead. Then at the 773 K, the reaction began to occur. As the increasing of temperature, the reaction gone further. The peaks of PbO and C weaken constantly, while the peaks of metallic lead became stronger gradually. When the temperature was at 973 K, the peaks of PbO and C were still existed. So the reaction didn't go thoroughly till the 973 K. Compared with the thermodynamics calculation result, when the temperature is higher than 273 K, the reaction hadn't go. The reaction temperature needed up to 973 K even higher to react thoroughly. Consistent with the thermodynamics calculation, the product was metallic lead for the reaction between PbO and pulverized coal.

3.3. The first step to prepare CaS

In the two-step reactions between heavy metal gypsum and lead paste, the first step was to prepare CaS the reducing agent for the second step. In the previous study, the process for the preparation of CaS by heavy metal gypsum and pulverized coal was practiced. The reaction of $CaSO_4$ and pulverized coal was conducted at 1173 K in the tube furnace. Then the solid product was analyzed by XRD, and the XRD patterns just as Fig. 9 indicated. The residuals were mainly composed of CaS with bits of impurities such as CaF_2 which was from reaction reagents. In view of the patterns of the product, the residual was relatively pure, which can be attempted to use as the reducing agent in the second step.

The product CaS was the mediate product in the process of the decomposition of heavy metal gypsum to get CaO and SO_2. As a mediate product, it was relative unstable and the reducibility was strong, for this reason, calcium sulfide was relatively easily to react with lead paste.

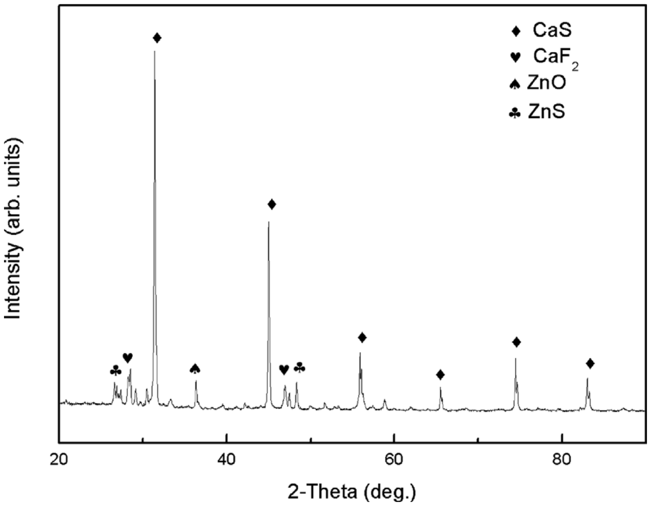

Fig. 9. The XRD patterns of product from the first step.

3.4. The reaction between CaS the product obtained from the reaction of heavy metal gypsum and lead paste directly

The product CaS from the first step was attempted to be used as a reducing agent to react with lead paste which was mainly consist of $PbSO_4$ and PbO. And the residual obtained was analyzed by XRD to determine the main phase components. According to the theoretic and experiment study of reaction temperatures and products, the reaction temperature of CaS and lead paste was chosen at 1073 K.

As shown as Fig. 10, the solid residual was composed of PbS and $CaSO_4$, in which PbS was the objective composition and $CaSO_4$ was not expected. Given the XRD patterns of the product, most of diffraction peaks were the peaks of PbS and a small amount peaks were the peaks of $CaSO_4$. And the generation of $CaSO_4$ was from the reaction between CaS and $PbSO_4$ as indicated as equation (8). The by-product $CaSO_4$ was derived from the reaction between $PbSO_4$ and CaS according to the investigate of the thermodynamics calculation and the experiments of $PbSO_4$ and CaS demonstrated too.

The generation of by-product $CaSO_4$ was not favored of the recycling of heavy metal gypsum. Because the first-step reactant

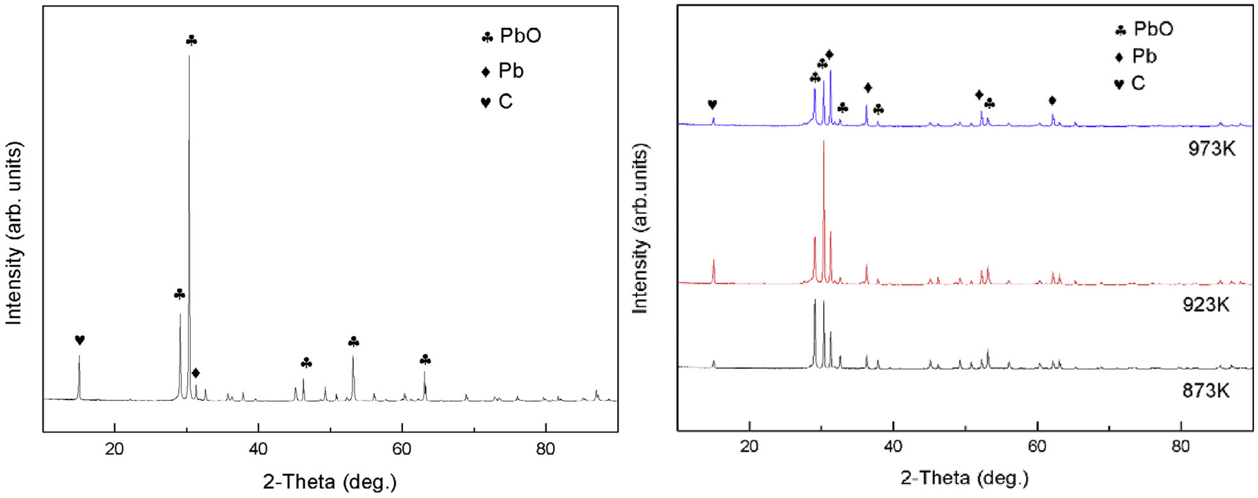

Fig. 8. The XRD patterns of reaction products at different temperature for the reaction between lead oxide and pulverized coal, a) was 773 K, b) were 873 K, 923 K and 973 K.

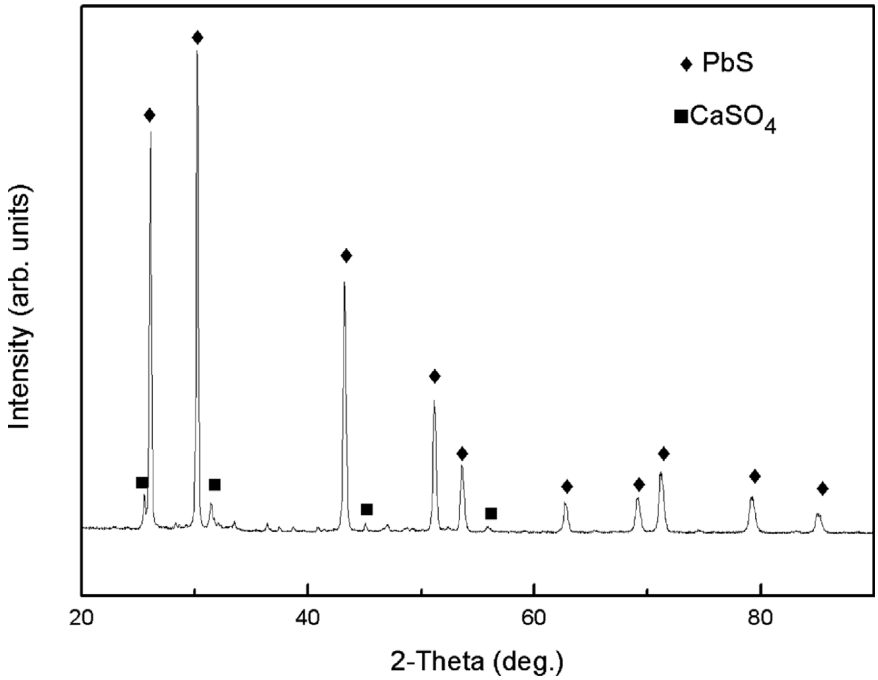

Fig. 10. The XRD patterns of the products from the reaction of $CaSO_4$ and lead paste.

agent $CaSO_4$ that the primary component of heavy metal gypsum was generated in the second-step again. And the by-product would accumulate constantly. Based on the study of the two-step reaction between heavy metal gypsum and lead paste, the recycling of heavy metal gypsum was feasible to preparation lead sulfide. In the process, the pulverized coal was proposed to add into the reaction to prevent the generation of $CaSO_4$. In our previous study pulverized coal could react with $CaSO_4$ from 973 K to 1373 K. So the pulverized coal may react with $CaSO_4$ to remove the by-product.

3.5. The effect of pulverized coal in the reactions between heavy metal gypsum and lead paste

For the generation of by-product $CaSO_4$, the two-step reaction between heavy metal gypsum and lead paste wasn't successful, and the by-product regenerated in the subsequent process for PbS. So, to prevent the generation of by-product $CaSO_4$, the pulverized coal was added into the two-steps reactions. There were three was designed to add pulverized coal into the reaction. The first design was to add excess pulverized coal in the first step to obtain more product CaS. And the second was to add excess pulverized coal at the beginning of the second step. In the third design, moderate pulverized coal was added in the third stage that separated from the second step.

In the same methods, the residuals were analyzed by XRD. And Fig. 11 was the XRD patterns of the products for the three schemes to add pulverized coal. As shown as Fig. 11, the main phase component was PbS. However, in the products of the first and the third designs for the addition of pulverized coal, the residual was considerable pure, in which PbS was the only phase component. And in the product of the second design, there were diffraction peaks of metallic lead which was not in favor of the recycling of element lead and easy to cause second pollution. So as far as the three designs, the first and the third was better than the second design according to the components of the residuals. On the other hand, according to the reaction cost, the first design was better than the third one.

In the two-steps reaction process, the first step was to prepare CaS to attempt to use as reducing agent in the second step. And the second step was to react with lead paste. Wherein the key reactions were the reactions of $PbSO_4$ and CaS, and PbO with CaS to obtain objective product PbS. And these reactions controlled the reaction rate. In addition, according to the thermodynamics calculation and experiments, the method using heavy metal gypsum and lead paste to prepare PbS was feasible. As far as the side reaction that generate $CaSO_4$ was not in favor of the recycling of calcium and sulfur resource, at the same time, the by-product was difficult to decompose. So the pulverized coal was added to prevent the generation of $CaSO_4$. As the method of the first design to add pulverized coal, the final products were mainly PbS with a small amount of metallic lead.

According to the residual of the first design, the percentage of lead in the product was concerned. To examine the percentage of lead accurately, the ICP-MS was adopted. In addition, comparing the percentage of lead in the reactant and residual that meant the loss rate of lead could be calculated as equation (9). As Table 4 shows, the percentage of lead were 68.47% and 70.98%, respectively. More important the content of lead in the final product satisfied the standard level of lead that was the industrial standard for the nonferrous industry of China. That meant the final product could be used as raw materials in the process of lead smelting. At the same time, heavy metals in heavy metal gypsum could be collected and accumulated in the recycling process.

Loss rate, E is calculated as equation (18):

$$E = \frac{m_1 w_1 - m_2 w_2}{m_1 w_1} \times 100\% \tag{18}$$

where w_1 and w_2 are the percentage of the lead in the raw material and the product, respectively. And calculating as equation (18), the loss rate of lead was 4.5%, which meant that a dust collection device was needed.

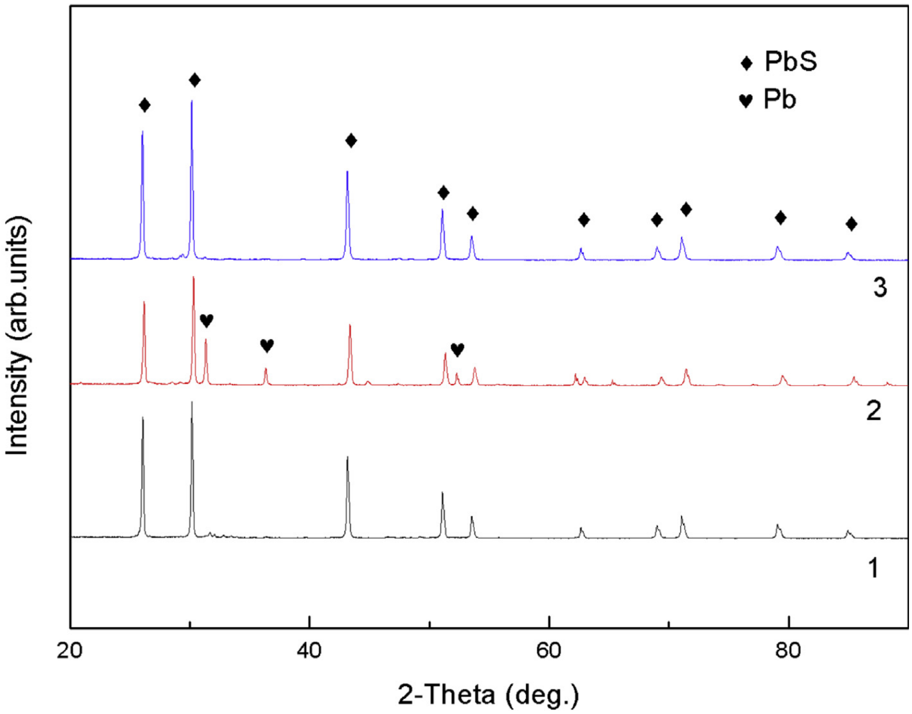

Fig. 11. The XRD patterns of the products from the two-steps reaction with pulverized coal.

Table 4
The content of lead in raw materials and residuals (wt.%).

Materials	Percentage of lead (wt.%)
Raw materials	68.47
residuals	70.98

4. Conclusions

The method with two-step reaction to synthesize PbS and generate CaO in this paper was proposed to recycle heavy metal gypsum and lead paste. In the first step, CaS was generated by reducing heavy metal gypsum with pulverized coal at 1173 K. Then CaS reacted with lead paste at 1073 K with some pulverized coal. The two reactions of $PbSO_4$ and CaS, PbO and CaS were key reactions and controlled the reaction of reaction rate. In the final product, PbS and CaO were the main components. And the content of lead in the final product was up to 70.89%, exceeding the standard level of lead of industry standard for the nonferrous industry of China, although the loss rate of lead was 4.5%. So the two-step product PbS could be used as raw materials in the lead metallurgical industry. At the same time, CaO could be reused to replace some slag forming constituent or recycled as smelting flux. In addition, heavy metals in heavy metal gypsum could be collected and accumulated in the cyclic process. In this way, heavy metal gypsum and lead paste could be recycled in an economic, environmental, high value-added method.

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