

THE MINERAL CONSTITUTION AND LEACHABILITY CHARACTERISTICS OF DUSTS FROM DIFFERENT LEAD SMELTING FURNACE

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Abstract

The lead smelting dusts contain complex composition such as Pb, Zn, Cd, S and As, which pose serious environment problem. This research used several physical and chemical methods to study the basic properties of different lead smelting dusts including blast furnace dust, reduction furnace dust, reverberatory furnace dust and bottom blowing furnace dust. The results of characterization showed that these dusts have different phases, element composition and surface morphology. In addition, the distribution of elements and compounds presented a certain trend, which will impact the leachability of their major elements. At the same time, leaching experiments were carried out on the four types lead smelting dusts to provide leachability information for metal recovery.

Introduction

The world lead production in 2012 was 10.56 million tons, among which China contributed 43 % of the total lead production. Being the largest lead producer and consumer in the world [1], China produced 4.54 million tons of lead concentrates in 2013 according to the data released by the China nonferrous metals industry association [2,3]. While more than 80% of lead is produced by traditional sintering, roasting, and reduction smelting process, which is a continuous oxidation and reduction process. In this process lead sulfide concentrate, flux, return dusts and dolomite or calcite lime are granulated first and then sintered at the temperature of 800°C in oxygen sufficient condition, followed by adding coke and return slag in reduction process to produce crude lead [4, 5]. There are obvious differences among the lead smelting dusts derived from different smelting process. Blast furnace dusts is produced from raw material sintering process in which galena is oxidized, which is collected after being treated in fuming furnace [6]. Reducing furnace dust is derived from reducing process of sinter slag, and metal oxide in slag is reduced into metal by carbon oxide and part of materials go into flue gas with rising airstream during the process. At the same time, part of lead stream would be secondary oxidized in the process of rising [7].

A reverberatory furnace smelting method has been carried out for reusing the low concentration SO₂ gas. A series of tasks including galena roasting, mutual reaction, melting slagging and refining containing liquation and impurities removal are completed in the same reverberatory

furnace. The process produces material containing 99% of Pb and a small amount of matte [8]. Besides, another method named bottom blowing oxidation process (SKS lead smelting method) aiming at solving SO₂ pollution problem was operated in the year of 2002 for the first time in China[9, 10]. The amount of bottom blowing furnace dust produced from the strong oxidation phase is huge due to inlet of oxygen-enriched air.

According to national list of hazardous waste, the lead smelting dusts are classified as dangerous pollutant because they contain lead, cadmium, arsenic and chloride compounds which are considered as primary or secondary pollutants[11, 12]. Besides, the production and storage amount of lead smelting dusts are huge, so these dusts cannot be recycled in the process because of contaminating the primary materials. These lead smelting dusts can lead to environment problem if discharged directly without adequate treatment.

Therefore, it is necessary to determine how to separate and recover these valuable elements from the dusts before discharge. Many comprehensive recovery methods have been developed by researchers in recent years. Fu et al [13] used a selective chlorination roasting method to remove fluoride and chloride from lead fuming furnace; Tang [14] et al investigated the zinc extraction experiments using ammonium sulfate solution at high temperatures; Turan et al [15] applied the method of concentrated sulfuric acid roasting followed with water to recover huge acid insoluble metals; Ruiz et al[16] prepared zinc oxide after dust being leached with ammonia. However, most objects of those researches were electric arc furnace dust [17-21], which has different chemical composition and mineralogical structure with lead smelting dusts, and there is few report about the characterization of lead smelting dusts. Therefore, it is necessary to study the chemical and mineralogical characterization of different kinds of lead smelting dusts for selecting the most suitable methods to recovery them.

Materials and Experiments

Dust characterization

The experimental samples were derived from four types of lead smelting dusts named blast furnace dust(D1), reducing furnace dust(D2), reverberatory furnace dust(D3)and bottom blowing furnace dust(D4)produced in JINLI lead smelting industry of Henan province. Before analysis, the samples were dispersed by ethanol. Blend samples evenly before sampling to ensure representativeness of samples. The chemical composition of dust samples were analyzed by X-ray fluorescence (XRF), which was focused on determination of specific elements such as lead, zinc, cadmium, sulfate, chloride, arsenic. Chemical titration analysis, atomic absorption spectrometry (AAS) and emission spectrometry by inductively coupled plasma (ICP) and ion exchange chromatography are also used to check the chemical compositions of dusts.

The structural characterizations of lead smelting dusts were performed through X-ray diffraction analysis in a Siemens appliance model D500. X-ray patterns of samples powdered to 400 mesh were obtained with monochromatic Cu K α radiation in the 2 θ -range from 10 $^{\circ}$ ~90 $^{\circ}$ at a scan rate of 1 $^{\circ}$ ·min $^{-1}$, and fixed counting time of 1s for each step. X-ray diffraction patterns were analyzed both visually and by the comparison technique using the Joint Committee of Powder Diffraction Standard (JCPDS) data. Use Jade 5.0 software to analyze detection results.

FTIR spectra were collected on a Model Nicolet iS5 FTIR. For each spectrum, 32 scans with a resolution of 2 cm $^{-1}$ between 4000 and 400 cm $^{-1}$ were used in transmission mode on KBr pellets made with 2mg sample and 200 mg KBr. It is aimed at analyzing surface adsorption group.

Scanning electron microscopy (SEM) with X-ray energy dispersive spectrometry (EDS) was performed to gain further knowledge of the lead smelting dust particles structure, morphology and their chemical composition..

Leaching Test

Leaching tests were carried out in a beaker immersed in a thermostatic water bath under mechanic agitation to keep solid particle suspended evenly. The water solubility and acid solubility of main elements in four dust samples were taken into account. Sulfuric acid was selected as leaching agent because it could separate lead from most acid-soluble ions. The effects of acid concentration (0-70 g/L), solid/liquid ratio (5:1-30:1), leaching temperature (25-80°C) and leaching time (5-30 min) on the elements content in leached residue were investigated. The major elements were analyzed for Pb, Zn, Cd, As, S and Cl in residue.

Results and Discussion

The elemental composition of dusts

Table I shows the chemical composition results of lead smelting dusts determined by X-ray fluorescence method. The elements presented in four dust samples were similar and the majority elements were lead, zinc, cadmium, sulfur, arsenic, and chlorine. The minor elements were iron, copper, aluminum, silicon, sodium and potassium. The amount of elements was different in four dust samples. The lead content in blast furnace dusts was relatively high because D1 was derived from the first step of raw materials treatment so that partial of materials would volatilization. Major metals in reduction furnace dusts were lead, zinc and cadmium. Chlorine content was relatively high due to the volatilization of chloride under high temperature and reducing atmosphere. The major elements of reverberatory furnace dust were lead, zinc, cadmium, iron, copper and sodium, because they were produced from a continuous process of raw material treatment to remove impurities. Owing to lead and cadmium sulfide or sulphate were served as bottom blowing furnace raw materials, the major elements in D4 were lead, cadmium and sulfur, and zinc content was relatively lower than the other three dust samples.

The results of individual metal content analysis in four dusts point to the need of examining its physical and chemical properties since it is considered to be a type of industrial waste. Moreover, special attention will be given to the content of major elements in water or acid leachates in order to find a proper solution for their recovery. As seen from Table 1, it is better to recycle lead, zinc and cadmium from D1 and D2; and there is more economical advantage to recycle lead and cadmium from D4; besides, it is more difficult to comprehensively recycle elements from D3 due to its complexity.

Table I. The chemical composition of lead smelting dust (%)

Element	Pb	Zn	Cd	S	As	Cl	Fe	Cu	Si	Al	Na	K
D ₁	61.84	12.21	9.67	7.91	1.85	2.16	0.40	0.12	0.13	0.05	1.05	2.74
D ₂	37.75	26.38	14.04	5.36	2.56	8.79	0.19	0.14	0.14	0.07	<0.01	2.74
D ₃	49.87	3.38	6.71	7.58	0.03	1.05	2.13	2.13	0.64	0.03	12.03	<0.01
D ₄	39.92	0.27	34.49	18.79	<0.01	3.68	0.07	0.26	0.01	0.04	0.27	<0.01

The mineralogy structure and chemical compound of the dusts

The X-ray diffractograms of D1, D2, D3 and D4 samples can be seen in Fig.2, which mainly displays the diffraction peaks of lead, zinc and cadmium compounds labeled with black, blue and red numbers. According to data of card JCPDS, the main identified phases are shown in TableII.

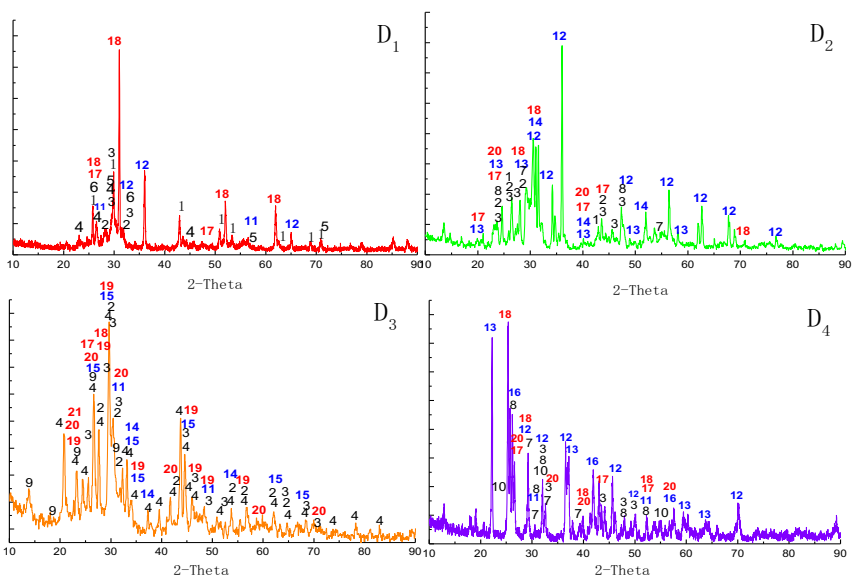


Figure2. XRD patterns of four lead smelting dusts. (1 PbS, 2 Pb₂O₃, 3 Pb₅(AsO₄)₃Cl, 4 PbSO₄, 5 Pb₇O₈Cl₂, 6 PbAs₂S₄, 7.PbO, 8 Pb₃O₄, 9.Pb₂O(SO₄), 10 PbO₂, 11 ZnS 12 ZnO, 13 Zn₃(AsO₄)₂, 14 ZnAs, 15 Zn₃As₂, 16 CdO, 17 CdS, 18CdAs, 19 Cd₂As₂Cl₂, 20 CdSO₄, 21 Cd₃(AsO₄)₂)

The forms of lead compounds in D1 were complex, and among those lead sulfides was the most obvious phase. Zinc sulfide and zinc oxide identified as the minor phases could not be unambiguously confirmed due to the superimposition of their diffraction peaks with those of major peak. The presence of cadmium arsenide could be ascertained due to the consistency of major diffraction peak, but cadmium sulfides and sulfates might not be unambiguously confirmed. D2 was came from the reducing process of sintering slag, so most of lead and zinc compounds were oxide. Besides, lead sulfide, zinc arsenic and zinc arsenate could be identified in minor peaks. Cadmium sulfide and cadmium arsenic were identified as the main cadmium species in D2. The main major phase identified in D3 was lead sulfate, and lead sulfide, clinomimetite, lead oxides were also possible existed in it. Zinc arsenate identified as major phase could not be confirmed because of the superimposition with lead sulfate diffraction peak. The presence of cadmium compounds were the most complex, such as cadmium sulfide, cadmium arsenic, cadmium arsenic chloride, cadmium sulfate, cadmium arsenide. D4 was

derived from the strong oxidation process of raw materials, so the lead sulfide or lead arsenic could not be found from Fig.2. The diffraction peaks of zinc compounds were covered by other strong peaks because of minor zinc content. Cadmium oxide was confirmed to be the major phase in D4. Besides, cadmium sulfide and sulphate could not be ruled out because they had those major phases like XRD pattern.

Table II. Results of phase analysis of lead smelting dusts samples

sample	Identified phase										
	1	2	3	4	5	6	7	8	9	10	11
	PbS	Pb ₂ O ₃	Pb ₃ (AsO ₄) ₃ Cl	PbSO ₄	Pb ₃ O ₈ Cl ₂	PbAs ₂ S ₄	PbO	Pb ₃ O ₄	Pb ₃ O(SO ₄)	PbO ₂	ZnS
D ₁	●	○	○	○	○	○	○	×	×	×	○
D ₂	○	○	○	×	×	×	○	○	×	×	×
D ₃	○	○	×	●	×	×	×	×	○	×	○
D ₄	×	×	×	●	×	×	○	○	×	○	○
sample	Identified phase										
	12	13	14	15	16	17	18	19	20	21	
	ZnO	Zn ₃ (AsO ₄) ₂	ZnAs	Zn ₃ As ₂	CdO	CdS	CdAs	Cd ₂ As ₂ Cl ₂	CdSO ₄	Cd ₃ (AsO ₄) ₂	
D ₁	○	×	×	○	×	○	●	×	○	×	
D ₂	●	○	○	×	×	●	○	×	○	×	
D ₃	×	×	×	×	×	○	○	×	○	○	
D ₄	○	×	×	×	●	○	×	×	○	×	

* (●) Identified phases in major peak (○) Identified phases in minor peak (×) Phases undetected

In general, the lead smelting dusts were composed of metal oxide, sulfide, sulphate, arsenic, arsenate and chlorine-containing compounds. Not all the identified phases in minor peaks displayed in TableII were confirmed in the diffractogram due to the superimposition of their diffraction peaks with those of the more abundant phases.

The infrared spectra of D1~D4 samples can be seen in Fig.3. All the spectra presented a broad band around 3460cm⁻¹ due to O-H stretch of hydrogen bonded water. D4 displayed the strongest O-H stretch vibration [17, 22]. All the four spectra displayed a band around 1640 cm⁻¹ assigned to a vibration of the water molecule [22], which were surface absorbed or entrapped in cavities. It could be found water molecule content in D4 was the highest, but few could be identified in D2. A weak absorption peak near 779 cm⁻¹ was attributed to SiO₂[23], which is an impurity phase of quartz. The vibration degrees of SiO₂ were related to the silicon content in dusts, so the vibration of D₃ was the strongest. Seen from the spectrum of four dusts, it could be presumed that the band located around 1120 cm⁻¹ is due to a sulfate (SO₄²⁻) vibration, being the other strong sulfate vibration, expected around 617 cm⁻¹[18]. It could be found that sulfate content in four dusts was in the order of D₄ > D₃ > D₂ > D₁. The bands around 500 cm⁻¹ were assigned to vibrations of simple oxides[24] such as lead oxide, zinc oxide and cadmium oxide. The vibration in D₂ was most obvious, which could be speculated to be caused by ZnO and PbO according to TableII. Although no sulfur was expected in the spectra, sulfide could not be ruled out in dusts.

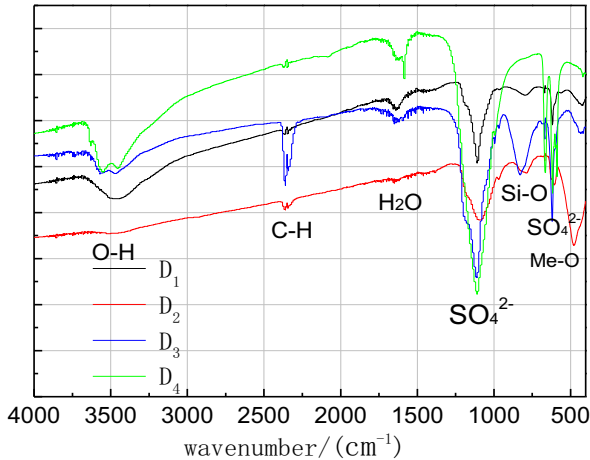


Figure 3. FTIR spectra curves of lead smelting dusts samples prepared as KBr

Microstructure of the dusts

SEM micrographs of D1, D2, D3 and D4 samples can be seen in Fig.4. The grains in four samples have displayed various different morphology such as spherical, block, cubic crystalline structure and some irregular non-crystalline state. It is reported that the formation of dusts undergoes two steps: first, the emission of dust “precursors” (vapors, metal droplets, and solid particles) inside the furnace; second, the conversion of those precursors into dusts through agglomeration and physic-chemical transformations [17].

As seen from Fig.4 D1a~b, the particle size of D1 was between 0.1~1 μ m, which was smaller than the data detected in granular analyses. It can be seen from D1a~b that particles distribution of D1 was even and most of them displayed spherical structure, which indicated that they have been formed from the liquid state after evaporation condensation or volatilization of fine particle. The white substance in Fig.4 D1c whose EDS elemental analysis pointed to zinc oxide was wrapped by black fine particle aggregates assigned to lead compounds and next to grey substance assigned to cadmium sulfide. The microstructure of D2 observed in Fig.4 D2a~c indicated that the size distribution range was wide and particle forms were various. The spherical shapes of granules with Pb and O as major elements were assigned to lead oxide phase. The cubic particle whose EDS analysis pointed to lead sulfide was derived from the unreacted raw material. As shown from D2b, particles were wrapped or agglomerated. The fine particles being wrapped were mainly composed of zinc oxide and cadmium sulfide through EDS analysis. The spherical shapes were the main microstructure of D3 seen in Fig.4 D3a~c. The granules were mixture of zinc, cadmium, copper, iron and sodium compounds identified by EDS analysis. The distribution of phase was relatively homogeneous in D3c, because reflecting smelting process was continuous so that dust component was diverse and mixed. The microstructure of D4 observed in Fig.4 D4a-c was irregular sintering phase, indicating the granules have undergone sinterization during fly off from the molten metal to the bag filter. The amorphous phase identified as sulfate was formed by reaction of metal oxide and rapidly released SO₂.

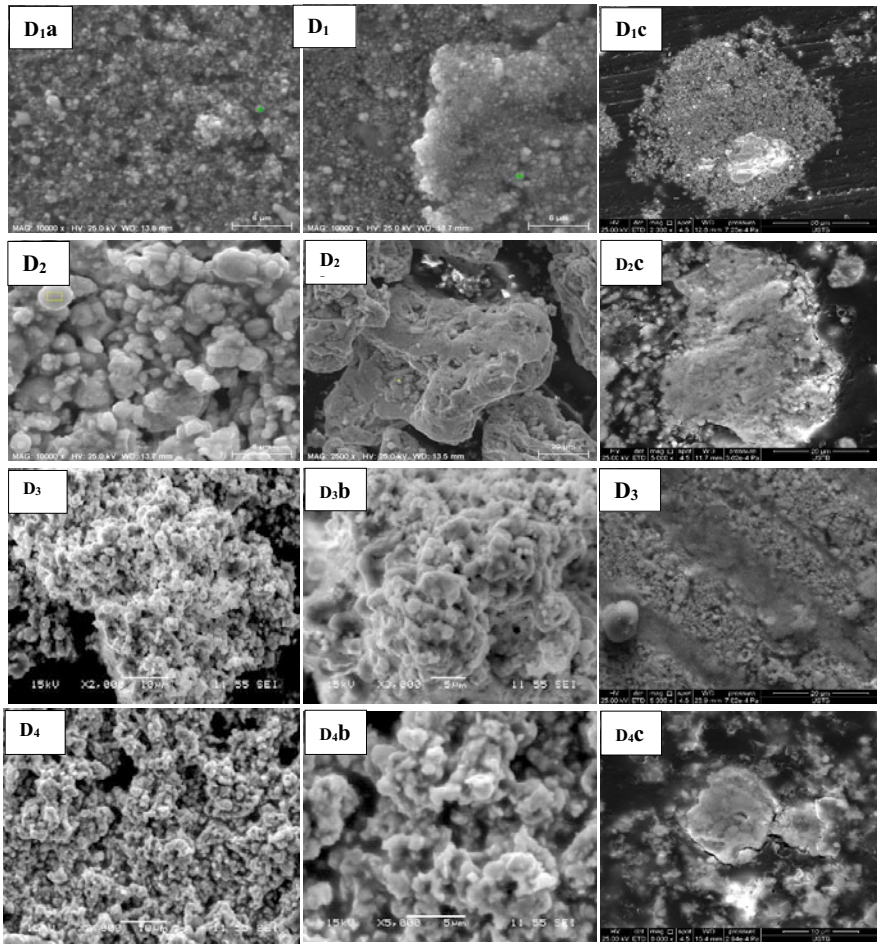


Figure 4. Microstructure photos of four lead smelting dusts

The leachability of the different dusts

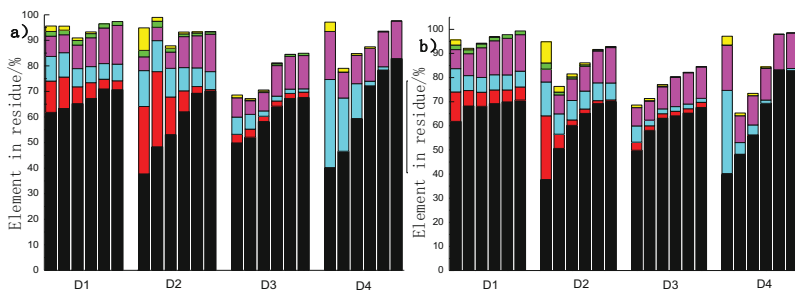
Considering sulfuric acid can easily dissolve a large part of elements from dusts, the experiment of ions leachability of dusts was carried out in sulfuric acid solution. As seen from Fig.5a~d, the first column of each dust presents the elements content in dust before leaching.

Fig 5a indicates the effect of sulfuric acid concentration on elements content in the residues. With acid concentration increasing, zinc content in D₁ and D₂ were significantly decreased. When acid concentration reached 70 g/L, zinc in D₂ was totally leached, while zinc in D₁ and D₃

were just leached 54.8% and 42.9% respectively. The leached amount of cadmium in D₄ was affected by acid concentration obviously, and cadmium was totally leached as acid concentration reached 70 g/L, besides, the cadmium in D₁, D₂, D₃ were reduced about 38.2%, 40.5% and 80.4% respectively at the same concentration. As partial particles of D₂ were wrapped shown in Fig.4 D₂b, the wrapped arsenate (Zn₃ (AsO₄)₂) would be released with dissolution of zinc and cadmium. The arsenic has dissolved 17.3% in D₁ and 63.7% in D₂ at the concentration of 70 g/L. The effect of leaching time on elements content in the residues is shown in Fig 5b. The chloride ions were totally removed from four dusts between 5 and 10 min. The ions leaching rate of D₁ was relatively fast due to a considerable part of compounds were insoluble sulfide and the leached amount of zinc, cadmium and arsenic reached 54.6%, 38.1%, 14.6% in 5 min. It took 30 min to leach whole zinc from D₂, while just 51.25% of cadmium and 87.5% of arsenic were removed at most. On the other hand, it just needed 10 min to obtain the largest removed amount of zinc and cadmium from D₃, but increasing time to 30 min was beneficial to increase the lead content in residue due to the complexity of elements. It only took 20 min to totally leach cadmium from D₄.

Fig. 5c shows the effect of leaching temperature on the elements content in residue. Increasing temperature was beneficial to remove cadmium, zinc, arsenic and chloride from four dusts at different extent. It can be seen from Fig. 5c that 60°C was considered as optimum leaching temperature, and higher temperature did adversely affect the leaching result because of water evaporation. As seen from Fig.5d, liquid solid ratio of 20:1 could be selected as proper parameter for leaching D₁, D₂ and D₄, because soluble compounds were relatively less in D₁ and particle sizes of D₃ and D₄ were relatively small. However, increasing liquid solid ratio to 30:1 was better to reach the optimal ions leaching amount of D₂.

Above all, combined with characterization results of dusts, all the chloride ions could be removed from dusts. Besides, 17.3% and 63.7% of arsenic identified as arsenate could be removed from D₁ and D₂ respectively. About 54.5% of leached zinc from D₁ was contributed to dissolution of zinc oxide, and about 38.2% of cadmium from D₁ was derived from cadmium sulphate and cadmium oxide. As to ions leachability of D₂, all zinc could be totally leached, which was identified as soluble zinc oxide, and 40.5% of leached cadmium was contributed to cadmium sulphate. About 42.9% of zinc came from arsenate could be leached from D₃, and 80.4% of cadmium derived from sulphate and arsenate could be also removed from D₃. The cadmium existed as cadmium oxide and cadmium sulphate in D₄ could be totally leached at optimal conditions.



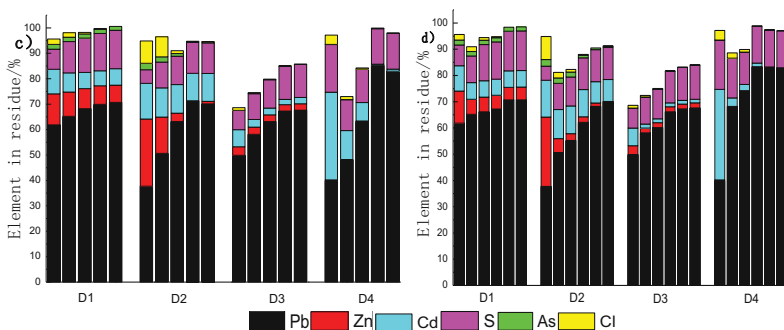


Figure 5. The effects of different leaching conditions on the elements content in leached residue: a) acid concentration (from left to right: elements content in dusts, treated with water, 10g/L acid, 30g/L acid, 50g/L acid, 70g/L acid); b) leaching time (from left to right : elements content in dusts, 5min, 10min, 15min, 20min, 30min); c) leaching temperature (from left to right : elements content in dusts, 25 °C, 40 °C, 60 °C, 80 °C); d) liquid to solid ratio (from left to right : elements content in dusts, 5:1, 10:1, 15:1, 20:1, 30:1).

Conclusions

The characterization results of four lead smelting dust samples show that there are obvious differences in chemical composition, particle size distribution, phase composition and microstructure among four studied samples. D₁ contains high amount of lead and unoxidized sulfides and arsenides because it was obtained from the first step of treating raw materials. Most of lead and zinc compounds in D₂ were oxides for sintering slag as the material. It is more difficult to recycle elements from D₃ due to its chemical complexity. As for D₄, cadmium content was relatively high and almost all cadmium compounds were oxides and sulphates. In order to obtain the highest leaching efficiency when using sulfuric acid as reactant, the appropriate leaching conditions were determined as follows: acid concentration of 70g/L (for four dusts), leaching temperature of 60°C (for four dusts), leaching time of 5 min (for D₁), or 30min (for D₂, D₃), or 20min (for D₄), liquid to solid ratio of 20:1 (for D₁, D₃, D₄) or 30:1 (for D₂).

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