SULFIDATION TREATMENT OF PLATING SLUDGES AND MOLTEN INCINERATION FLY ASHES FOR RECOVERY OF HEAVY METALS

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SULFIDATION TREATMENT OF PLATING SLUDGES AND MOLTEN INCINERATION FLY ASHES FOR RECOVERY OF HEAVY METALS

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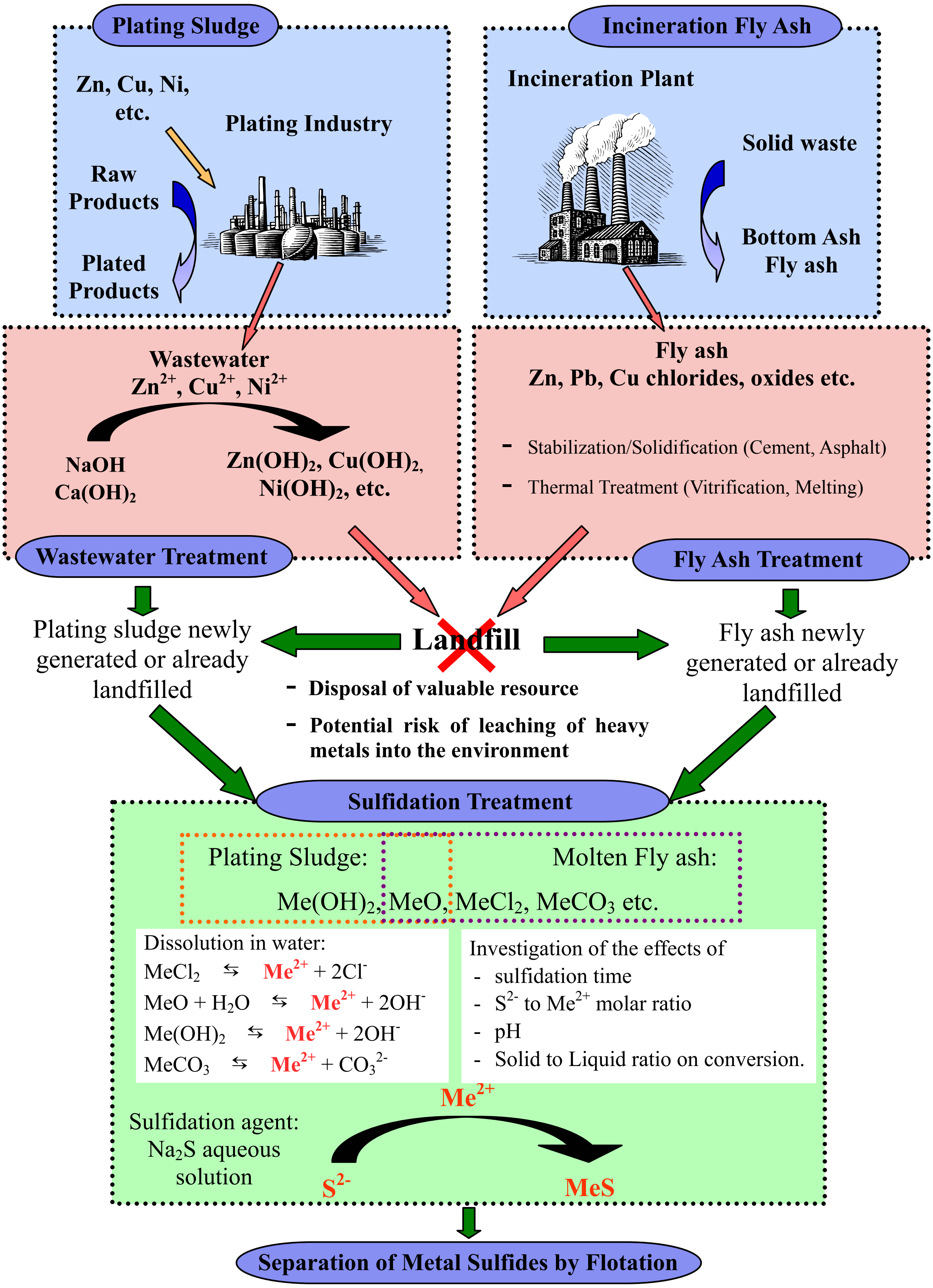
CHAPTER 1

Introduction



1.1 Sustainable development

One of the most commonly cited definitions of the sustainable development states that the sustainable development is "economic development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs" [1]. Meanwhile, the sustainable development can also be defined as "the kind of human activity that nourishes and perpetuates the historical fulfilment of the whole community of life on Earth" [2]. Basically, the sustainable development aims at developing people (child survival, life expectancy, education etc.), economy (wealth, productive sectors and consumption) and the society (institutions, social capital and states), while sustaining nature (Earth, biodiversity and ecosystems), life support (ecosystem services, resources and environment) and community (cultures, groups, places and regions) [3].

When further considering the goal of sustaining the life support, the need for preservation of energy and material resources is clearly of great importance. From the energy demand point of view, the presently used energy resources such as fossil and nuclear fuels are classified as finite energy resources, while the only permanent energy supply on Earth is the solar energy. Thus, if sustainability is to be achieved, a development of new technologies capable of capturing the solar energy is required to meet the energy demand of human society in case that presently used energy resources are depleted. By contrast, all material resources are limited to the present global supplies and therefore recycling of material resources is an inevitable requirement to accomplish the goals of sustainable development. The material resources recycling is not a new process and the sustainable recycling of the material resources has been going on Earth for about four billion years. However, during the last few centuries, this natural recycling system has been adversely affected by the technological progress of human society [4]. In order to counteract the adverse impacts of the technological progress on the natural recycling system, a better understanding of the natural recycling system as well as the effects of human activities on the natural recycling is necessary. One of the ways of deeper understanding of this recycling system includes an evaluation of the flows of various materials through the environment and the construction of so called material cycles.

1.2 Material flows and material cycles

The number of various natural materials exploited by human society has significantly increased since the time of industrial revolution, which ensued from enormous progress in the development of technologically advanced society. These materials, including engineering metals, are derived from natural deposits such as rocks; sediments etc., and prior to their actual use as useful products; these raw materials usually undergo a transformation process. Subsequently, at the end of life cycle, eventually a large fraction of these materials is returned to the environment [5]. The flows of these materials through the environment are commonly described using material cycles. The material cycles have their origin in biogeochemistry and they are composed of reservoirs – the compartments in which the material can be stored and the material flows termed as material fluxes.

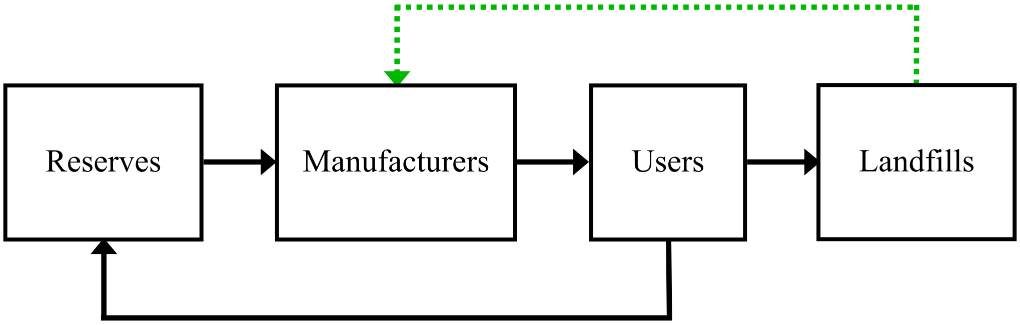


Fig. 1.1: Four reservoir model of an anthropogenic open cycle [5]

An example of simple four-reservoir model of an anthropogenic open cycle is given in **Fig. 1.1** [5]. The cycle consists of the mobilization of raw material resources from geological reserves, the material transformation during manufacturing, utilization of manufactured materials/products by users, recycling of spent material/products and disposal of spent materials/products to a landfill [5]. The most important thing to be noticed is that the first reservoir (Earth's crust) continuously supplies raw material, while the last reservoir continually receives it. The term landfill used in this figure for the last reservoir implies not only actual landfill as a repository for anthropogenic material, but also includes terrestrial sediments, ocean sediments, seawater etc. The landfill represent an accumulative reservoir, which means that the cycle shown in the

Fig. 1.1 remains opened (cycle is not in balance). In order to bring this cycle into the balance, an introduction of a material flux from accumulative reservoir of landfill to manufacturers or reserves compartments is an essential requirement. Example of such additional material flux (dashed green line in the figure) was added to the cycle to express the need for recycling of spent materials which are presently being disposed of to landfill sites.

1.3 Metal cycles

This dissertation thesis focuses on the recovery of heavy metals of zinc, lead, copper and nickel from industrial waste such as plating sludges and incineration fly ashes, and hence only metal cycles of these four metals will be further discussed in terms of mobilization, transformation, utilization in useful applications and disposal.

1.3.1 Mobilization

As shown in **Fig. 1.1**, the materials-heavy metals are at first mobilized from the first reservoir (Earth's crust). The mobilization itself can be divided into natural mobilization, which constitutes of mobilization of heavy metals by plants and by sea spray, and anthropogenic mobilization which is composed of heavy metals ore mining as well as coal and petroleum mining. Subsequently, to determine the mobilization, the average concentration of each metal in coal, petroleum, crust, seawater and dry plants are required and the values used by Klee and Graedel [5] are given in **Table 1.1**. Further, Klee and Graedel [5] used the annual mining production of each metal [6], worldwide consumption of fossil fuels of 4741 Tg/yr [7], biomass burning of 8600 Tg/yr [8], suspended sediment flux of 1500 Tg/yr, expressing crustal weathering [9], sea spray of $2\text{x}10^{11}$ Mg/yr [10] and plant primary production of 224,500 Tg/yr [11] and they estimated the annual anthropogenic and natural mobilization, as shown in **Table 1.2**. In this table, the total mobilization of heavy metals is divided into anthropogenic mobilization (mining, fossil fuel burning and biomass burning) and to natural mobilization (crustal weathering, sea spray and plant primary production) [5].

Table 1.1: Mobilization factors used in mobilization calculations [5]

Element	Average concentration in coal [g/Mg]	Average concentration in petroleum [g/Mg]	Average concentration in crust [g/Mg]	Average concentration in seawater [g/Mg]	Average concentration in dry plant [g/Mg]
Cu	15	0.4	14	0.001	10
Pb	40	0.3	17	0.00004	2.7
Ni	20	66	19	0.001	3.0
Zn	50	0.8	52	0.8	45

Table 1.2: Calculation of mobilization rates and dominance [5]

	Anthropogenic mobilization				**Natural mobilization**				**Mobilization summary**	
Element	Mining [Gg/year]	Fossil fuels [Gg/year]	Biomass burning [Gg/year]	Total [Tg/year]	Crustal weathering [Gg/year]	Sea spray [Gg/year]	Plant primary production [Gg/year]	Total [Tg/year]	Total [Tg/year]	Anthropogenic as % of total
Cu	13,200	72	86	13	21	0.2	2,245	2.3	16	85
Pb	3,100	191	23	3.3	26	0.01	606	0.6	3.9	84
Ni	1,250	311	26	1.6	28	0.5	673.5	0.7	2.3	69
Zn	8,730	240	387	9.4	78	293	10,103	10	20	47

In **Table 1.2**, it can be seen that the anthropogenic mobilizations represent 47%, 84%, 85% and 69% of total mobilizations of zinc, lead, copper and nickel, respectively. Furthermore, the anthropogenic mobilizations can be almost completely attributed to the mining activities since mining represents 92%, 94%, 99% and 78% of total anthropogenic mobilizations for zinc, lead, copper and nickel, respectively. To briefly conclude this part, we can say that with an exception of zinc, the anthropogenic mobilization plays a major role in heavy metals mobilization [5].

Finally, an interesting relation between anthropogenic mobilization and solubility of a particular chemical form of element in water was discovered by Klee and Graedel [5] as shown in **Fig. 1.2**. In particular, the heavy metals, which are generally present in the nature either as relatively insoluble metal oxides (oxide ores) or metal sulfides (sulfide ores) [12], were characterized by a much higher contribution of anthropogenic mobilization to the total mobilization in the environment than sodium and potassium which are typically present as easily soluble sodium and potassium chlorides.

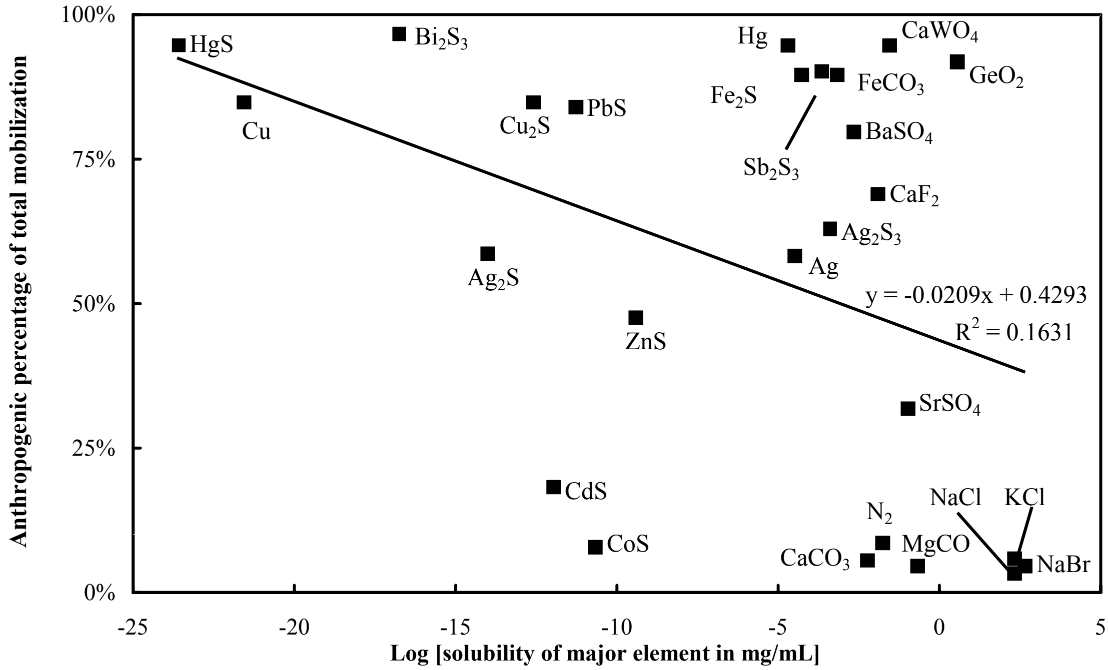


Fig. 1.2: Plot of anthropogenic mobilization against the aqueous solubility of common chemical forms of elements in nature [5]

1.3.2 Refining of heavy metals

As mentioned in Section 1.3.1, heavy metals are mainly present in the crust either as metal sulfides or metal oxides. In the case of zinc and lead, the respective principal metal ores are sphalerite (ZnS), which accounts for 90% of zinc production, and galena (PbS) [13,14]. Concerning copper ores, either copper sulfide or oxide ores are presently mined. Among numerous copper sulfide minerals, chalcopyrite ($CuFeS_2$), covellite (CuS), chalcocite (Cu_2S), bornite (Cu_5FeS_4), enargite (Cu_3AsS_4) and tetrahedrite ($(CuFe)_{12}Sb_4S_{13}$) are the most widely exploited. Meanwhile, chrysocolla ($CuSiO_3$), malachite (Cu_2CO_3), azurite ($Cu_3(CO_3)_2(OH)_2$) and cuprite (Cu_2O) are the predominant copper oxide minerals [15]. Finally, nickel is in the nature present in either magmatic sulfide ores such as pentlandite $(Ni,Fe)_9S_8$ mined underground or in lateritic hydrous nickel silicates and garnierites, which are surface mined [16,17]. The content of heavy metals in presently mined ores is reported to be quite low and usually varies in the range of 1 to 10% for zinc, 1 to 5% for lead [18], 0.5 to 1.0% for copper [19,20] and 1 to 4% for nickel [16].

After extraction (mining), the ores are ground and subjected to a subsequent beneficiation process of desirable minerals. In the case of sulfide ores, flotation, which has already been used for more than hundred years, is reported to be still the most modern, the most efficient, and the most widely applicable technique for separation of metal sulfides from tailings. Flotation is based on the highly specific attachment of particles of one desirable mineral or group of minerals, suspended in a solution containing various flotation additives, to air bubbles. Consequently, the bubbles (with mineral particles attached) are consequently brought to the surface and collected to achieve separation of desirable mineral from tailings [21-23].

The froth flotation is the most important separation technique in the processing of lead and zinc ores and its effectiveness depends on four major factors related to the nature of ore body: the degree of oxidation of the ore, the abundance of iron sulfides, the presence of copper minerals, and the basic or acidic nature of tailings [14,24]. Similarly, in copper ore processing, about 75% of total amount of copper is concentrated from copper minerals using the froth flotation [15,25]. After flotation, the concentrate is subjected to smelting and refining processes before the "pure" metal is finally obtained. As an example, a typical flow sheet for copper metal production is shown in **Fig. 1.3**.

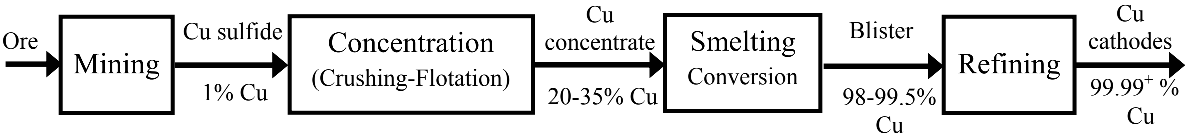


Fig. 1.3: Simplified diagram for the pyrometallurgical route in copper production [19]

1.3.3 Use of heavy metals

Copper: Copper is characterized as one of the most important metals owing to its durability, ductility, malleability, and electrical and thermal conductivity. Copper is used primarily as the pure metal or in alloys such as brass, bronze, gun metal, and "Monel metal" (an alloy of nickel and copper and other metals (such as iron and/or manganese and/or aluminium). The copper metal and copper alloys are used in constructions, electrical and electronic products, transportation equipments, industrial machinery and equipments, and consumer and general products [26]. It is reported that a small percentage of copper production goes also into the manufacture of copper compounds, mainly copper sulfate. Copper sulfate is used in agriculture, metal finishing, mineral froth flotation, wood preservatives, and for water treatment [26].

Lead: The commercial importance of lead is a result of its ease of casting, high density, low melting point, low strength, ease of fabrication, acid resistance, electrochemical reaction with sulfuric acid, and chemical stability in air, water and soil. The primary use of lead is in the manufacture of lead-acid storage batteries, including SLI (Start, Light, Ignition) batteries used in cars, trucks, and other vehicles and industrial type lead acid batteries. Further, lead is utilized in other applications such as alloys used in bearings, brass and bronze and some solders; sheets and pipe for nuclear and X-ray shielding; cable covering; noise control materials; chemical resistant linings; ammunition; pigments and lead compounds used in glass making, ceramic glazes, plastic stabilizers, caulk, and paints [27].

Nickel: Nickel is primarily used in alloys because it imparts to a product such desirable properties as corrosion resistance, heat resistance, hardness, and strength. Nickel alloys are often divided into categories depending on the primary metal with which they are alloyed and their nickel content. Nickel salts are used in electroplating, ceramics, pigments, and as catalysts. Sinter nickel oxide is used as charge material in the manufacture of alloy steel and stainless steel. Nickel is also used in nickel-cadmium (NiCd) and nickel-metal hydride (NiMH) batteries. Among these applications, the highest amount of nickel is consumed in the production of stainless steel and heat-resistant steel followed by the production of nickel-copper and copper-nickel alloys, electroplating etc. [25].

Zinc: The primary use of zinc metal is as a protective coating of other metals, such as iron and steel. In general, the protective coating is achieved by various methods including hot-dip galvanizing, continuous-line galvanizing, electro-galvanizing (electroplating), zinc spraying, and painting with zinc-bearing paints. Further, zinc metal is frequently alloyed with other metals (e.g., aluminium, copper, titanium, and magnesium) to impart a range of properties and zinc alloys are used for casting and wrought applications, dye-casting, construction, and in other alloys (e.g., brass and bronze) which may be found in electrical components of many household goods. In addition, zinc compounds such as zinc oxide have dental, medical, and household applications [28].

1.3.4 Production and consumption of heavy metals

The consumption of heavy metal has exponentially increased from the beginning of the industrial revolution owing to the fast development of an advanced society. **Figure 1.4** shows the increase in the world mine production (so called primary production) of heavy metals of copper, lead, nickel and zinc. In details, it can be seen that the primary production of copper and zinc steeply increased over the last decade, while the productions of lead and nickel were relatively stable over the last several decades.

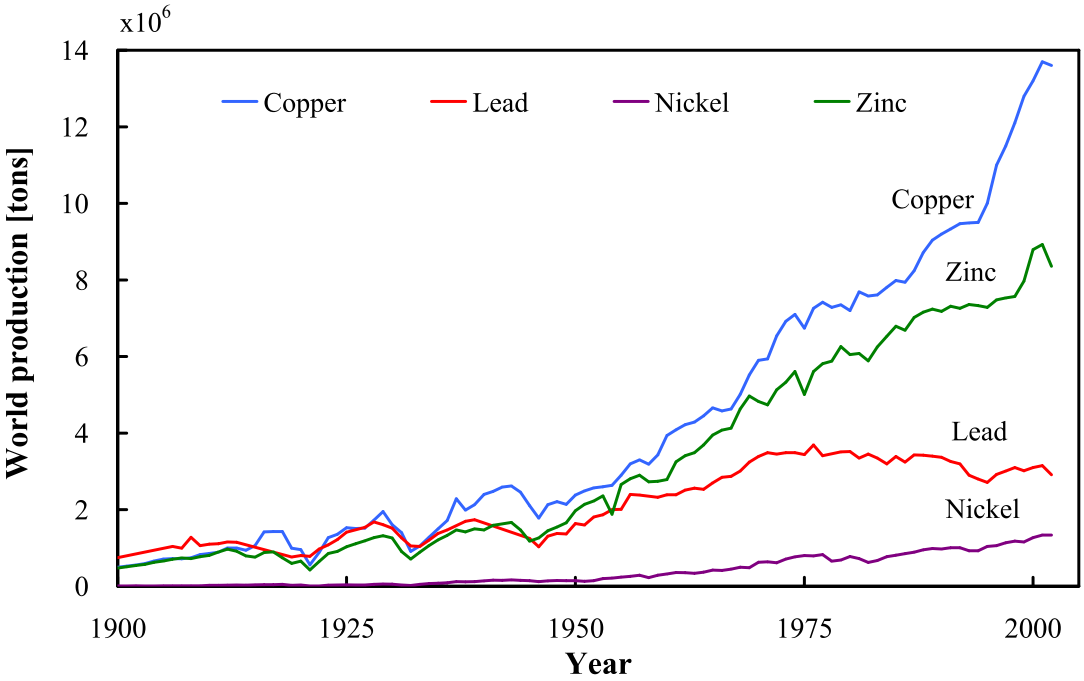


Fig. 1.4: World primary production of heavy metals [6]

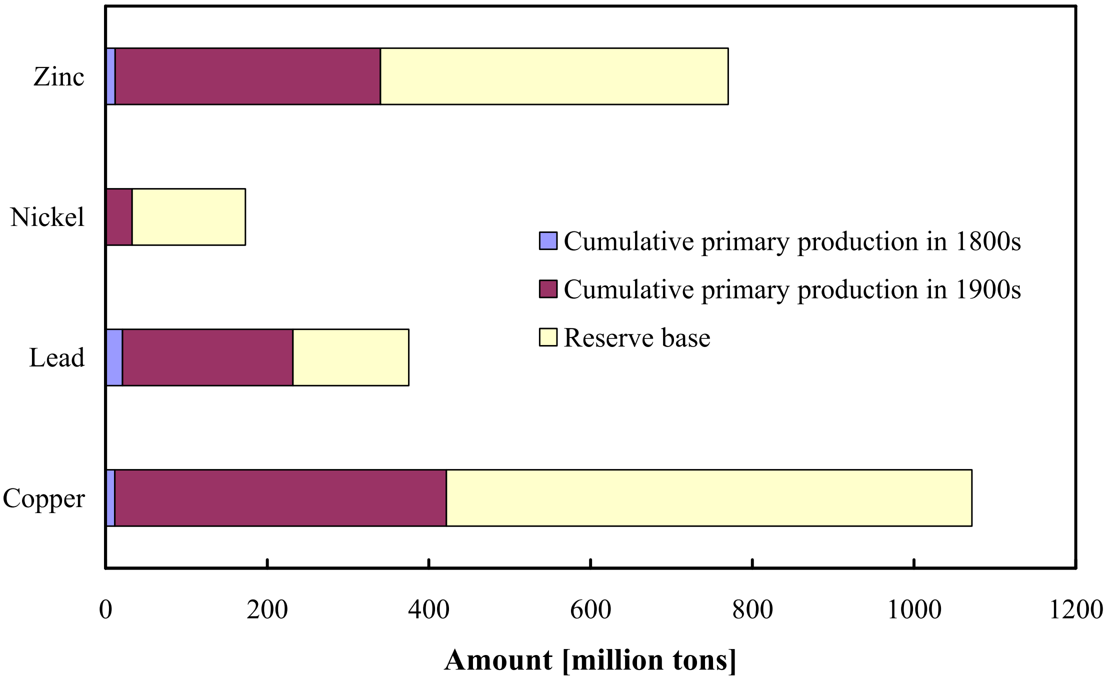


Fig. 1.5: Cumulative primary production and reserve bases [30]

The exact values of primary production vary from source to source and the values given in references [6] and [29] for the year of 2002 were as follows: the primary production of copper, zinc, lead and nickel amounted to 13.6 million tons, 8.36 million tons (8.89 million tons according to reference [29]), 2.91 million tons (2.83 million tons according to reference [29]) and 1.34 million tons, respectively [6].

Generally, the world consumption of heavy metals is much higher than the mine production (primary production) of heavy metals and the deficit in the primary production is balanced by the metal recycling (so called secondary production). For instance, in 2002, the total productions of zinc and lead were 9.71 million tons and 6.67 million tons, respectively. Meanwhile, the total world consumption of zinc was 9.38 million tons and the total world consumption of lead was 6.65 million tons [29].

Figure 1.5 shows the world primary production compared with the world reserves in a long-term picture for the heavy metals of copper, lead, nickel and zinc. The productions given in this figure are cumulative primary productions in 1800s and 1900s, while the reserve base is defined as a part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth [30,31]. It should be noted that much of the primary production has been incorporated in long-life products, many of which will ultimately be recycled back into the supply-chain. However, just with an exception of lead, in whose case the secondary production is already more important than primary production, recycling (secondary production) is very unlikely to meet the world's annual needs for metal. This implies a continuous need for discovery and development of new sources of supply as well as development of advanced recycling technologies to increase the secondary production [30].

Based on the world primary production and data available on reserve bases, an estimation of reserve lives of copper, lead, nickel and zinc was attempted by several researches. **Table 1.3** shows the estimation of reserve lives of these heavy metals as given in literature [30,31]. Given the estimations in this table, it can be concluded that the heavy metals reserves would be depleted within this century, which increases the need for heavy metals recovery/recycling.

Table 1.3: Estimated reserve-lives of selected heavy metals

Heavy metal	Reserve base [million tons]¹⁾	Reserve life [years] ¹⁾	Reserve base [million tons] ²⁾	Reserve life [years] ²⁾
Cu	650	35	610	61
Pb	143	41	120	43
Ni	140	50	110	100
Zn	430	36	330	46

1) cited from Reference [30] (the estimation based on data from ILZSG – International Lead and Zinc Study Group, ICSG – International Copper Study Group and INSG – International Nickel Study Group)
2) cited from Reference [31] (the estimation was based on data from US Geological survey, 1997)

1.3.5 Recycling: physical and chemical separation

As discussed in previous section, the natural deposits of heavy metals would be soon depleted and therefore, a recycling system should be developed to decrease the need for primary production of heavy metals and to achieve as complete cycling of heavy metals as possible. Presently, the metal recycling system generally focuses on collecting “pure” metals and metals alloys from end-use products, such as vehicles, construction waste (electrical and plumbing systems, heat exchangers and so on), electrical appliances etc. [31]. After collection, the metals are simply re-melted and combined with primary refined metal. The process is relatively simple, but a complete recycling of metals is not accomplished. Consequently, the metals are disposed of to landfill sites, as a part of municipal or industrial waste.

Furthermore, the metals are many times collected in the form of a mixed waste stream and thus a separation of desirable metals is required. The presently used separation processes are basically divided into physical and chemical separation.

Physical Separation of ferrous and nonferrous metals, including copper, lead nickel and zinc, from mixed waste stream is based on differences in physical characteristics such as density and electromagnetic properties to separate metals from other materials and from one another. A high efficiency can be achieved using physical separation and the metals recovered in such a manner are classified as secondary metal source [31].

Chemical separation can be used to recover heavy metals from many kinds of industrial waste such as wastewaters, waste liquors, solid waste etc. Among these, the wastewaters and waste liquors are considered to represent the majority of industrial waste subjected to chemical separation. The efficiency of metals recovery depends on the metal concentrations in the wastewaters/waste liquors, properties of the solvent (pH, viscosity), and also on the presence of other metals and chemicals in wastewaters/waste liquors [32]. The actual recovery from wastewaters/waste liquors is achieved by chemical precipitation, ion-exchange techniques or membrane technologies [31]. In addition, Wernick and Themelis [31] also reported that standard hydrometallurgical as well as pyrometallurgical processes can be used to remove metals from some industrial wastes.

1.3.6 Recycling of copper, lead, nickel and zinc

Copper: In 1999, the Division for Sustainable Development of the Department of Economic and Social Affairs of the United Nations reported that copper recycling fluctuated in the range of 35% to 41% over the period of 1976 to 1997 [33]. Similarly, in 1996, Henstock [34] reported that the overall efficiency of copper recycling from waste was about 50% which also indicated that an enormous amount of copper was lost from the economy. The copper missing in Henstock's statistics was supposed to be either still in use (thus unaccounted for the statistics), lost into waste disposal (landfills) or dissipated [34]. The current waste disposal into the landfill includes for example the disposal of treated or untreated municipal and industrial waste to landfills (including plating sludges), the disposal of incineration residues (treated or untreated) of municipal and industrial solid waste etc. Finally, regarding the dissipated copper, presently dissipative uses of copper include agricultural applications as well as corrosion and about 5% of all copper wasted is dissipated in a way that contributes to contamination of soils [35,36].

Lead: The fact that the main utilization of lead is in automotive industry in lead-acid batteries significantly contributes to the highest recycling efficiency of lead among the other metals [37]. Worldwide, the storage batteries account for more than 60% of total lead consumption, while the lead recycling was reported to reach a value of about 50% in 1997 (after steady increase from about 30% in 1976) [33]. The strong relation between lead utilization in storage batteries and lead recycling is further illustrated on the example of the United States, where in 2003, 84% of lead was used in manufacturing the storage batteries. Meanwhile, it was also reported that 81% of refined lead production in 2002 was recovered from recycled scrap, among which the primary source was represented by recycled lead-acid batteries [27]. Another applications of lead involves utilization of lead and lead compounds in pipes; wiring; painting industry (pigments, anti-fouling paints); glass, ceramics and pottery (coatings, paints); plastics (inorganic filler in fire-retardant plastics, stabilizing agents) etc. [27]. The recovery of lead from these "additional" applications is undoubtedly much complicated due to the variety of products resulting in the losses of lead from economy, for example in the form of various household and industrial waste etc. In particular for household waste, Jung *et al.* [38] reported that lead was distributed in this waste as follows: 37% bulky waste, 33% paper/textile/plastics, 29% incombustible waste and 1% plastic packaging [38].

Nickel: The International Nickel Study Group estimated that about 25% of nickel is recycled worldwide [39], while the majority of nickel recycled comes from metal products (stainless steel, nickel plate, alloys etc.). However, a minor part of stainless steel and other nickel-containing items discarded by households and commercial establishments is also landfilled, or incinerated along with normal commercial and municipal waste. Another source of nickel loss from economy is the electroplating industry, where the nickel containing rinsing wastewater is discharged. Typically, nickel is removed from electroplating wastewater by the treatment with hydroxide, lime, and/or sulfide to precipitate a corresponding metal compound. The plating sludges generated in the treatment of plating wastewater are mainly disposed to a landfill site, since the recovery of heavy metals from mixed metal plating sludges by smelting was reported to be difficult due to the sludge heterogeneity as well as the presence of inorganic salts. Finally, ion exchange and adsorption techniques using activated carbon, activated alumina, and iron filings are also used for treating nickel-containing rinsing wastewater [25,40].

Zinc: Based on the data provided by International Lead and Zinc Study Group, the zinc recycling was estimated to reach only about 8.4% in 2002 [29], which seems to be in good agreement with the estimations of zinc losses from the economy. It is reported that about 70% of total zinc losses from the economy originated from the corrosion of zinc coating used as protection against corrosion on the steel products (plating). Another 15% of losses were attributed to the wear of tyres, which contain about 2% of ZnO [13]. Henstock, in his work on recycling of non-ferrous metals, concluded that the recycling of zinc is an extremely complex subject due to the variety of chemical forms (metallic and non-metallic) in which zinc is used [34]. Similarly, Gordon *et al.* [13] reported that the factors limiting zinc recycling are the difficulty of removing zinc from steel before re-melting, the loss of zinc from electric arc steel making furnaces, and the cost of recovering zinc from furnace dust. Further, no method of recovering zinc from rubber tyres has been found, and it is often difficult to separate zinc die-cast parts from automobiles [41]. The difficulties in zinc recovery results in zinc losses through various waste streams including municipal solid waste, construction and demolition waste, waste from electrical and electronic equipment, end of life vehicles etc. [13,42].

From the above given data, it seems to be clear that the recycling of heavy metals is not yet sufficient and should be further improved to prevent the depletion of heavy metal resources in the near future. At first, an improvement can be undoubtedly accomplished through an improvement of collection and separation methods of heavy metals from all kinds of municipal and industrial wastes. Second, a new recovery ways should be studied to recycle heavy metals involved in industrial and municipal wastes such as plating sludges, or incineration residues remaining after thermal treatment of municipal and industrial solid wastes, since these wastes represent major sources of heavy metals losses from economy.

1.4 Plating industry: generation and disposal of plating sludges

Metal plating is one of the many metal finishing processes which are basically divided as follows:

- cleaning (solvent cleaning, aqueous cleaning, abrasive cleaning, ultrasonic cleaning etc.)
- chemical and electrochemical conversion coatings (changing or converting the surface layer to impart various properties to the surface)
- plating (electroplating of various types of metals onto metal surfaces)
- other metallic coating (including hot dipping and mechanical plating)
- organic and other non-metallic coating
- stripping (removal of previous metallic coatings from parts or removal of coatings from articles that have to be reworked) [43].

Generally, metal finishing processes involve treatment of a metal work-piece in order to modify its surface properties, impart a particular attribute to the surface, or produce a decoration. Plating is a subset of such finishing operations that involves putting a coating of metal over a base metal substrate to give various desirable properties to the object. Metal coating is another subset of finishing operations and involves the application of paint or powder coating to a metal work-piece. Products from metal finishing operations can range from structural steel to jewellery [43].

The overall reasons to carry out a metal finishing process are summarized as follows:

- decoration
- protection against corrosion,
- providing resistance to oxidation, high temperatures, or UV radiation
- imparting mechanical properties, such as resistance to fatigue, improvement of ductile strength, or longevity
- resistance to the use of abrasives
- imparting electrical and thermal properties such as semi-conduction, thermal resistance, fire resistance, etc. [43].

In Japan, plating represents an important part of metal finishing processes and the plating industry annually consumes 6,054 tons of zinc; 5,732 tons of copper; 4,079 tons of nickel; 1,398 tons of chromium; 1,394 tons of tin as well as 80 tons of silver and 8,939 kilograms of gold to achieve desirable properties of products [44]. However, as well as many other useful processes, electroplating also generates various wastes, such as rinsing wastewaters, plating sludge, other chemical waste including spent bathes, cleaning liquors etc. [43].

1.4.1 Copper, nickel and zinc plating

Copper plating: Copper plating can be divided into several groups according the initial copper source such as copper cyanide plating which uses copper in the form of cuprous cyanide [$CuCN$], which must be complexed with either potassium or sodium cyanide to form soluble copper compounds in aqueous solutions. Copper cyanide plating baths typically contain 30 g/L of copper cyanide and either 59 g/L of potassium cyanide or 48 g/L of sodium cyanide. Other types of baths used in copper plating include copper pyrophosphate and copper sulfate baths. Copper pyrophosphate [$Cu_2P_2O_7$] plating, which is relatively non-toxic, is used for plating of plastics and printed circuits, but requires more control and maintenance of the plating baths than copper cyanide plating. Copper pyrophosphate plating baths typically contain 53 to 84 g/L of copper pyrophosphate and 200 to 350 g/L of potassium pyrophosphate. Copper sulfate [$CuSO_4$] baths are more economical than copper pyrophosphate baths, in terms of preparation and operation, and are used for plating of printed circuits, electronics and plastics as well as for electroforming and decorative purposes. Copper sulfate plating baths typically contain 195 to 248 g/L of copper sulfate and 11 to 75 g/L of sulfuric acid [45].

Nickel plating: Nickel plating is used for either decorative, engineering or electroforming purposes. Typically, the nickel plating baths contain a nickel source at a concentration varying from 60 to 84 g/L, and boric acid used as a catalyst at a concentration range from 30 to 37.5 g/L. In addition, in the case of decorative nickel plating, organic agents such as benzene disulfonic acids, benzene trisulfonic acid, benzene sulfonamide, formaldehyde etc. are added to the plating baths [45].

Zinc plating: The most widely used zinc plating solutions are categorized as acid chloride, alkaline non-cyanide, and cyanide. The most widely used zinc alloys for electroplating are zinc-nickel, zinc-cobalt, and zinc-iron. Zinc plating baths contain 15 to 38 g/L of acid zinc chloride [$ZnCl_2$], 6.0 to 23 g/L of alkaline non-cyanide zinc (concentrated solution of ZnO and NaOH), or 7.5 to 34 g/L of zinc cyanide [$Zn(CN)_2$]. Acid zinc-nickel plating baths contain 120 to 130 g/L of zinc chloride and 110 to 130 g/L of nickel chloride [$NiCl_2$]. Alkaline zinc-nickel plating baths contain 8.0 g/L of zinc metal and 1.6 g/L of nickel metal. Acid zinc-cobalt plating baths contain 30 g/L of zinc metal and 1.9 to 3.8 g/L of cobalt metal. Alkaline zinc-cobalt plating baths contain 6.0 to 9.0 g/L of zinc metal and 0.030 to 0.050 g/L of cobalt metal. Acid zinc-iron plating baths contain 200 to 300 g/L of ferric sulfate and 200 to 300 g/L of zinc sulfate. Alkaline zinc-iron plating baths contain 20 to 25 g/L of zinc metal and 0.25 to 0.50 g/L of iron metal [45].

The heavy metals employed in electroplating are mainly deposited on the surface of electroplating products, but a part of these metals is discharged from the plating industry as rinsing wastewater. The rinsing wastewater contains soluble metallic salts at elevated concentrations and must be treated in order to remove dissolved heavy metals. In Japan, the concentrations of heavy metals must be reduced below the permissible limits of 3 mg/L and 5 mg/L for Cu and Zn, respectively [46]. For comparison, the daily permissible limits allowed for common metal finishing facilities discharging more than 38,000 litres of wastewater per day defined by the U.S. Environmental Protection Agency are 4.5 mg/L, 4.2 mg/L and 4.1 mg/L for Cu, Zn and Ni, respectively.

1.4.2 Treatment of rinsing wastewater

Presently, the heavy metals can be removed from the rinsing wastewater by chemical precipitation, in which the dissolved heavy metals are converted to insoluble hydroxides, oxides, carbonates or sulfides [47-50]. Further, ion exchange [51], adsorption, chelation [52] or combination of chemical precipitation with reverse osmosis, ion exchange or electrodialysis [53] can be used to reduce the heavy metal concentrations below the permissible limits. Among these techniques, the chemical precipitation is the most widespread and chemical precipitation is carried out using either NaOH or $Ca(OH)_2$, while the pH value is kept within the range of 9.20 to 9.50 for at least 15 minutes. As far as the pH value is kept in this range, the content of various heavy metals involved in mixed-metal wastewaters can be reduced below the permissible limits [47,48]. The precipitate (so called plating sludge) containing various metal compounds is then dehydrated [54], and solidified with a stable binder in order to prevent the heavy metals from dissolving in the landfill sites [55]. As solidification binders, cement, lime, fly ash [56-58] and asphalt emulsions are usually employed [59].

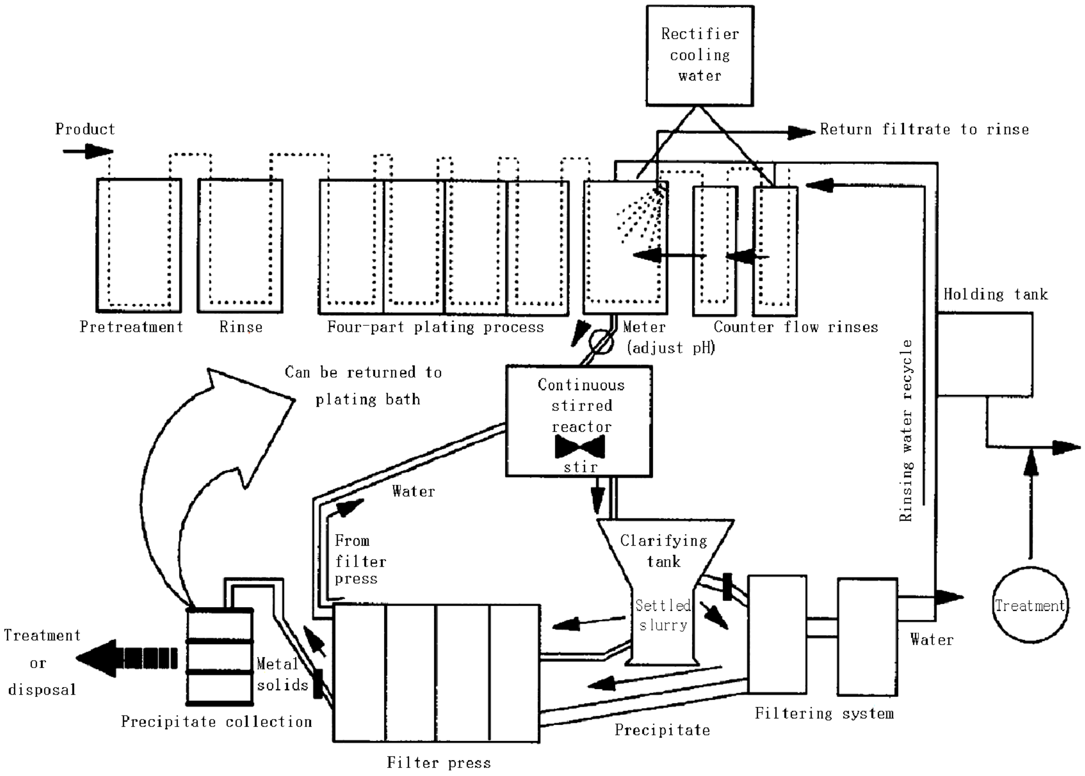


Fig. 1.6: Flow chart of non-cyanide zinc plating line equipped with recovery/recycle system [60]

The actual plating procedure, including the treatment of rinsing wastewater, varies according to the initial metal source (metal cyanide, chloride, sulfate etc.), type of plating (acid or alkaline) as well as according to particular plating shop. **Figure 1.6** shows a flow chart of an alkaline non-cyanide zinc plating shop equipped with the system for reuse of recovered chemical [60]. In this plating shop, dissolved zinc was precipitated as zinc hydroxide. The efficiency of zinc hydroxide removal from plating wastewater was reported to be 84% and approximately 30% of recovered zinc hydroxide was recycled to the plating baths leaving about 70% of zinc hydroxide for further treatment or disposal.

1.4.3 Composition of plating sludges

The treatment of plating wastewater brings about a generation of a large amount of plating sludges, which in Japan amounts to 65,000 tons/year. For a comparison, an amount of approximately 150,000 tons/year of plating sludges was generated in EU countries (before the EU expansion in May 2004) [61]. Generally, the sludges are classified as hazardous waste basically due to the presence of heavy metals. The concentrations of heavy metals vary from plating shop to plating shop, which results from various plating procedures used.

Magalhaes *et al.* [61] have attempted to classify the sludges using 39 samples of plating sludges from different plating shops and, in their work, the plating sludges were divided into five main groups. The average composition of the sludges from each group is given in **Table 1.4**. When the contents of heavy metals of zinc, copper and nickel are compared with those in presently mined ores, which vary from 1 to 10% zinc, 1 to 5% lead [18], 0.5 to 1.0% copper [19,20] and 1 to 4% nickel [16], it can be seen that with an exception of Group III, the content of these heave metals is higher in plating sludges than in mineral ores. Therefore, from the viewpoint of environment protection as well as conservation of metal resource, a development of effective systems for recycle and reuse of the metals involved in plating sludges is required.

Table 1.4: Elemental composition of plating sludges [61]

	Metal content [%]							
	Al	Ca	Cu	Cr	Fe	Ni	Zn	Total
Group I	0.30	2.34	0.25	0.78	39.3	1.29	11.7	55.97
Group II	0.39	1.47	0.73	4.22	6.66	0.57	28.4	42.41
Group III	35.4	0.69	0.01	1.03	0.16	0.06	0.01	37.40
Group IV	3.28	5.70	0.98	4.28	1.66	0.91	1.18	17.99
Group V	0.40	0.08	3.91	5.27	0.43	36.03	2.26	48.39

Group I – sludges processed with $FeCl_2$
Group II – sludges from Zn-plating processes
Group III – sludges from Al-anodizing processes
Group IV – sludges from mixed/multiple processing/plating operations
Group V – sludges from Cr-plating for decoration processes

1.5 Incineration of solid waste: generation and treatment of fly ashes

The currently used waste treatment methods of solid waste strongly depend on the type of waste and these methods are aimed to achieve the following objectives:

- to destroy the total organic matter content
- to destroy contaminants
- to concentrate inorganic contaminants
- to reduce the mass and volume of the waste
- to recover the energy content of the waste
- to preserve raw materials and resources [62].

This dissertation thesis deals with the treatment of molten incineration fly ashes either from municipal solid waste incinerator or automobile shredder residue incinerator. Hence, the detailed information is provided only on these two kinds of waste.

1.5.1 Municipal solid waste (MSW)

The generation of municipal waste in selected countries in 2000 was reported to be 760 kg *per capita* of municipal waste in the United States of America, 560 kg in the United Kingdom, 540 kg in Germany, and 410 kg in Japan [63]. The total amount of municipal solid wastes generated annually in Japan is about 50 millions tons and more than 70% of municipal solid waste produced is incinerated to decrease its volume [64], while the incineration residues (bottom ash and fly ash) represent 7-20 wt% of the original waste [65]. The incineration residues contain heavy metals such as Zn, Pb, Cu, Sn, Cr and Cd at elevated concentrations, and therefore, the incineration residues are classified as a hazardous waste. The content of heavy metals in the incineration residues is strongly dependent on the composition of the waste incinerated and on the type of incinerator. Jung *et al*. [65] divided the waste input into three main categories: (1) combustible waste (usually representing more than 90% of the waste feed), (2) shredded bulky waste, and (3) other (sludge, plastics, incombustible waste). In their work, it was found that the content of heavy metals in the incineration residues increased with an increase in the amount of shredded bulky waste input (composed of various wastes such as plastics, textiles, plastic films, paper, power cords, electric circuit boards, cans, rubber and wood).

1.5.2 Automobile shredder residues (ASR)

The automobile shredder residues (ASR) are the fraction obtained from the process of shredding end-of-life-vehicles, after recovery of iron and steel by magnetic separation. In Japan, approximately 5 millions vehicles are discarded every year, which results in a generation of 9.09 millions tons of automobile shredder residues and most of these residues are disposed of to a landfill site [66]. Similarly, in European Union, 75% of the total weight of end-of-life-vehicles is recycled, but the remaining 25% of so called automobile shredder residues is disposed of to a landfill because of its complexity [67]. Alternative treatment way to landfilling is the energy recovery process at municipal incinerator, cement kiln or blast furnace. The ASR contain more than 40% of plastics, 21% of elastomers, 10% of textiles, 3% of ceramic and electric materials (3%), and 5% of paint protecting coating. Concerning the heavy metals, ASR contain Zn and Cu at a concentration of about 1%, Pb at a concentration of about 0.25% and less than 0.05% Cd and Cr [67,68].

1.5.3 Treatment of incineration residues

Presently, the incineration residues from the thermal treatment of either municipal solid waste or automobile shredder residues are commonly disposed of to landfill sites and various pre-treatment techniques are carried out to prevent the heavy metals from leaching into the environment. Among the pre-treatment techniques, the stabilization/solidification with hydraulic binders [69], asphalt [70] or asphalt emulsion [71] are the major treatment ways. The stabilization/solidification techniques are relatively cheap and are based on the reduction of leachability of heavy metals by the formation of impermeable matrix enclosing the toxic heavy metals inside this matrix. However, the stabilization/solidification techniques also increase the amount of waste disposed of to landfill sites and no heavy metals recovery is carried out. Therefore, various extraction techniques using either acidic or alkaline medium have been investigated to achieve the heavy metals recovery [72,73].

Besides, thermal treatments such as vitrification [74], melting or sintering are applied to prevent heavy metals from the leaching to the environment. In Japan, the vitrification and melting processes are preferred by many municipal incineration plants due to the volume reduction of residues, decomposition of dioxins, reuse of molten residue and the reduction of metal leachability [75].

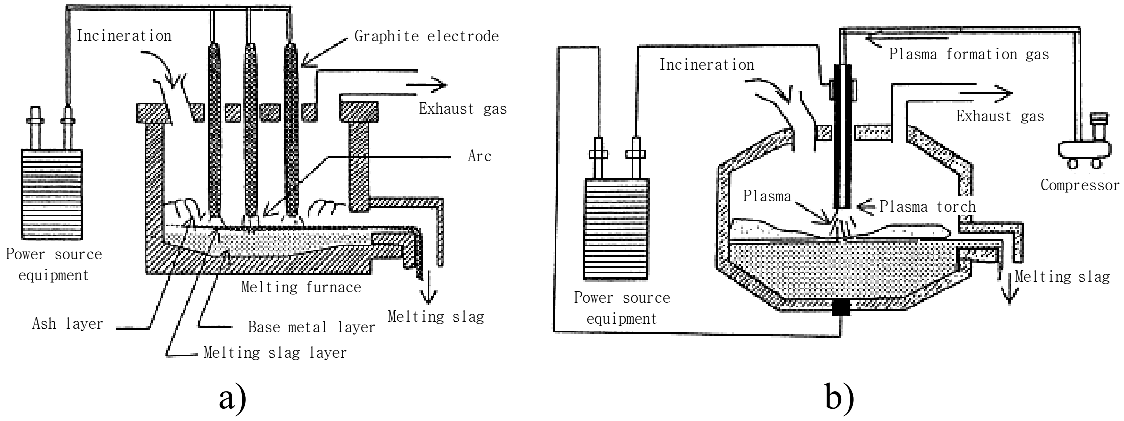


Fig. 1.7: Electric-arc melting furnace (a) and plasma melting furnace equipped with single torch (b) [76]

Basically, the melting processes can be divided into two groups: fuel-burning process (such as surface melting furnace, coke-bed melting furnace etc.) and electric melting processes (such as electric-arc melting furnace, plasma melting furnace etc.) [76]. **Figure 1.7** shows an electric-arc melting furnace and plasma melting furnace equipped with single torch [77]. In addition, a gasification-melting process which integrates gasification process at lower temperature (under oxygen atmosphere) with the melting process of residual solid matter (bottom ash and fly ash) can also be used and this treatment process has become popular in Japan [65,75].

After melting, the incineration residues are not rendered completely harmless and so called molten incineration fly ash (MFA), which contains considerable higher amounts of heavy metals such as zinc, lead and copper than incineration fly ash (IFA), is generated. **Table 1.5** shows the concentration ranges of zinc, lead and copper in the incineration fly ashes and bottom fly ashes (input of melting processes), concentration ranges of zinc, lead and copper in molten incineration fly ashes and slag (output of melting processes). As a comparison, the contents of these heavy metals in mineral ores are also given in this table.

Table 1.5: Content of Cu, Pb and Zn in incineration residues and mineral ores

	Cu [%]	**Pb [%]**	**Zn [%]**
Incineration fly ash (IFA)1)	0.04 – 0.25	0.10 – 0.34	0.43 – 3.3
Bottom fly ash (BA)1)	0.07 – 0.36	0.02 – 0.16	0.15 – 0.37
Molten incineration fly ash (MFA)2)	0.07 – 1.51	0.16 – 6.63	0.88 – 17.7
Slag2)	0.02 – 0.30	0.00 – 0.05	0.01 – 0.27
Molten incineration fly ash (MFA)3)	0.11 – 1.6	0.13 – 9.2	0.27 – 42.5
Metal contents in ores4)	0.5 – 1	1 – 5	1 – 10

1) Range of heavy metals content in IFA and BA as reported in [75]
2) Range of heavy metals content in MFA and slag as reported in [75]
3) Range of heavy metals content in MFA as reported in [77]
4) Range of heavy metals in mineral ores as reported in [18-20]

After melting, the molten incineration fly ashes are stabilized to prevent heavy metals from leaching and dispose of to landfills [76]. However, the recycling of heavy metals from molten incineration fly ashes should be targeted in the future, since the content of heavy metals is comparable to those of mineral ores.

1.6 Recovery of heavy metals

1.6.1 Plating sludges

McLay and Reinhard [40] reported that the number of companies interested in using metal-bearing sludges, such as smelters, as a feedstock in their manufacturing processes has recently increased, but actual recovery of heavy metals from the mixed metal sludge by smelting was found to be difficult. The reason lies in the fact that the metal finishing sludges contain a mixture of various heavy metals and are highly variable in composition. Furthermore, the metal sludges can also contain a significant amount of inorganic salts in the entrained water. In particular, halides are reported to be troublesome in a smelting process, most likely due to conversion of metals to metal chlorides, which are easily volatilized during smelting process and thus lost in the form of volatilized matter [40].

Nevertheless, several attempts have been performed to recover heavy metals from mixed plating sludges using various techniques. For example, Renard [78] reported that the efficiency of heavy metals leaching as high as 99% was achieved when heavy metals were leached from plating sludges using sulfuric acid. After leaching, heavy metals were precipitated using sodium sulfide at various pH values to achieve selective separation of heavy metals [78]. The heavy metal sulfides obtained can be consequently treated at smelters to obtained pure metals. In addition to metal leaching followed by sulfide precipitation [78], other recovery techniques such as metal leaching combined with electro-winning [79], solvent extraction [80] and pyrometallurgical and hydrometallurgical processes [81] have also been studied, but unfortunately the application of these processes has not proceed beyond laboratory scale.

1.6.2 Incineration fly ashes

For the heavy metals recovery from fly ash, various extraction techniques using mainly an acidic medium have been widely investigated. For instance, Katsuura *et al.* [72] reported that 35% HCl, 63% HNO_3 or aqua regia (a mixture of 35% HCl and 63%

HNO_3 at a ratio of 3:1) could be used to achieve a high extraction of heavy metals from fly ash. Similarly, Nagib and Inoue [73] found that 62.5 wt% Zn and 39.5 wt% Pb from incineration fly ash were extracted by 10 wt% HCl, while the same acid dissolved 94.0 wt% Zn and 77.0 wt% Pb from molten incineration fly ash. Further, in the case of 20 wt% acetic acid, 62.0 wt% Zn and 94.0 wt% Pb was extracted from incineration fly ash, and 97.0 wt% Zn and 98.0 wt% Pb from molten incineration fly ash. In the case of alkaline leaching with 3N NaOH followed by water washing, about 98.0 wt% Pb and 35.3 wt% Zn was dissolved from molten incineration fly ash. Finally, Nagib and Inoue [73] concluded that the acidic leaching was more effective than alkaline leaching due to a low solubility of Zn in an alkaline pH range; nevertheless higher purity of Pb and Zn leachate was achieved with NaOH [73].

After the extraction treatment, the heavy metals could be precipitated as metal sulfides, hydroxides, carbonates or chelates. Katsuura *et al.* [72] reported that, among the above mentioned precipitation techniques; the precipitation of heavy metals as heavy metal sulfides was comparatively better in terms of processing properties and cost. However, the precipitation of metal sulfides at pH range of 6.0 to 8.0 required various safety measures to prevent generation of poisonous H_2S gas. Subsequently, the precipitate formed could be subjected to heavy metal refining process at smelters. Okada *et al.* [77] reported that the heavy metals could be readily recovered from the precipitate by the imperial smelting process, in case that the precipitate contained at least 40 wt% Zn (there was no limit value for Pb) and not more than 0.2 wt% Cl, 3.5 wt% Si and 0.05 wt% Sn. However, if the content of undesirable elements of Cl, Si or Sn exceeds these limits, a dilution of the precipitate/treated fly ash with large quantity of ore is required [77].

1.6.3 Sulfidation treatment

When further considering heavy metals recovery at the smelters, it is necessary to remind that heavy metals are in the nature commonly present as sulfide ores such as galena (PbS), sphalerite (ZnS) or covellite (CuS). Prior to the smelting, the enrichment of heavy metals in these metallic ores is widely carried out by means of flotation technique [13]. Based on the currently used process of metal refining from natural ores, it is considered that the heavy metals involved in plating sludges or molten incineration fly ash may be directly converted to metal sulfides by mixing a plating sludge/fly ash with an aqueous solution of Na_2S. Subsequently, the plating sludge or molten incineration fly ash treated with Na_2S in such a manner could be subjected to separation of heavy metal sulfides formed, by means of a flotation technique, and subsequently to heavy metal refining process at smelters. Consequently, in the sulfidation treatment with Na_2S, the acid extraction pre-treatment and the possible generation of H_2S gas in the heavy metals precipitation step could be avoided. The sulfidation treatment of solid samples is not a completely new technology, since a similar approach has been already applied to improve flotation of various oxidized copper minerals such as chrysocolla, brochantite [82] and malachite [83,84]. Further, sulfidation process combined with flotation has been also studied for remediation of soil and sediments polluted with heavy metals such as cadmium, copper, lead and zinc [85,86].

In this work, sulfidation treatment of solid waste of plating sludges and molten incineration fly ashes was targeted as a possible way for heavy metals recovery. In the plating sludges, the heavy metals are present as metal hydroxides, metal oxides or various metal hydroxides sulfates while in the molten incineration fly ashes, metal chlorides or oxides are the prevailing chemical forms. Solubility data of metal chlorides, oxides, hydroxides, sulfates as well as sulfides are given in **Table 1.6**. Among the many chemical forms of heavy metals, the lowest solubility was observed for metal sulfide, which is in agreement with **Fig. 1.2**.

Table 1.6: Solubilities of Cu, Ni, Pb and Zn compounds [87,88]

Heavy metal	Compounds	Solubility at 25°C [g/100-water]	Solubility product constant at 25°C
Cu	$CuCl_2$	$44.6^{(1954)}$	-
	CuO	-	$1.5^{x}10^{-20\,(1956)}$
	$Cu(OH)_2$	-	$1.5^{x}10^{-20\,(1956)}$
	Cu_2S	-	$1.0^{x}10^{-48\,(1952)}$
	CuS		$8.0^{x}10^{-36\,(1952)}$
	$CuSO_4$	$18.2^{(1937)}$	-
Ni	$NiCl_2$	$39.6^{(1932)}$	-
	NiO	-	-
	$Ni(OH)_2$	-	$(1.0\text{-}1.8)^{x}10^{-16\,(1956)}$
	NiS	-	$2.0^{x}10^{-21\,(1952)}$
	$NiSO_4$	$41.2^{(1939)}$	
Pb	$PbCl_2$	$1.07^{(1929)}$	-
	PbO	-	$1.2^{x}10^{-15\,(1921)}$
	$Pb(OH)_2$	-	$1.1^{x}10^{-20\,(\text{at }22°\text{C};1952)}$
	PbS	-	$6.8^{x}10^{-29\,(1940)}$
	$PbSO_4$	$0.0045^{(1934)}$	-
Zn	$ZnCl_2$	$81.2^{(1905)}$	-
	ZnO [89]	-	$2.2^{x}10^{-17\,(1965)}$
	$Zn(OH)_2$	-	$4.0^{x}10^{-16\,(1950)}$
	ZnS	-	$8.0^{x}10^{-25\,(1952)}$
	$ZnSO_4$	$36.7^{(1940)}$	-

The latest data from the summary of solubility data [87,88] were chosen. The year of publication of the particular solubility data is given in the superscript.

The conversion of metal compounds to metal sulfides is supposed to start with the dissolution of heavy metals in water as shown in Eqs. (1.1) – (1.4), where Me stands for Cu, Ni, Pb or Zn.

$$MeCl_2 \leftrightharpoons \mathbf{Me^{2+}} + 2Cl^- \qquad (1.1)$$

$$MeO + H_2O \leftrightharpoons \mathbf{Me^{2+}} + 2OH^- \qquad (1.2)$$

$$Me(OH)_2 \leftrightharpoons \mathbf{Me^{2+}} + 2OH^- \qquad (1.3)$$

$MeSO_4 \leftrightharpoons \mathbf{Me^{2+}} + SO_4^{2-}$ (1.4)

In the subsequent step, the Me^{2+} ions released are precipitated with sulfide ions of sodium sulfide as expressed in Eq. (1.5).

$\mathbf{Me^{2+}} + S^{2-} \leftrightharpoons \mathbf{MeS}(s)$ (1.5)

As shown in this reaction mechanism, it is assumed that the conversion of metal compounds to metals sulfides proceeds through an ion exchange reaction, and thus the reaction rate is supposedly affected by the solubility of particular chemical form of heavy metal. At first, considering the conversion of highly soluble metal chlorides and sulfates, relatively high conversion rate of metal chlorides and sulfates to metal sulfides is to be expected.

By contrast, the solubility of metal oxides and hydroxides is generally quite low and the molar concentration of metals dissolved in distilled water is limited by K_{sp} (solubility product constant) of the particular metal **(Table 1.6)**. In the case of $Cu(OH)_2$, the maximum molar concentration of Cu^{2+} ions dissolved in distilled water is given by general formula Eq. (1.6).

$$K_{\mathrm{SP[Cu(OH)_2]}} = 1.5x10^{-20} = [Cu^{2+}]x[OH^-]^2$$

$$\Rightarrow [Cu^{2+}] = \sqrt[3]{\frac{1.5x10^{-20}}{4}} = 1.55x10^{-7}\,\mathrm{mol/L} \quad (1.6)$$

From this equation, it can be concluded that only limited amount of Cu^{2+} ions arising from dissolution is present in solution and the bulk part of copper hydroxide remains un-dissolved. However, if the free Cu^{2+} ions are removed from the solution by precipitation with S^{2-} ions, the dissolution of $Cu(OH)_2$ should continue. Similarly, a maximum molar concentration of Cu^{2+} ions dissolved in distilled water of in the case of metal sulfide of CuS can be determined using Eq. (1.7)

$$K_{\mathrm{SP[CuS]}} = 8.0x10^{-36} = [Cu^{2+}]x[S^{2-}]$$

$$\Rightarrow [Cu^{2+}] = \sqrt{8.0x10^{-36}} = 2.83x10^{-18}\,\mathrm{mol/L} \quad (1.7)$$

It can be seen that the maximum molar concentration of Cu^{2+} ions in the case of CuS is much lower than in the case of $Cu(OH)_2$, confirming that Cu^{2+} ions should indeed be removed from the solution as insoluble CuS. Thus, when $Cu(OH)_2$ is mixed with aqueous solution containing sulfide ions, the Cu^{2+} ions arising from the dissolution of $Cu(OH)_2$ are precipitated to establish the equilibrium conditions for CuS resulting from $K_{SP[CuS]}$. As a consequence of Cu^{2+} ions removal, further dissolution of $Cu(OH)_2$, driven by equilibrium conditions for $Cu(OH)_2$ occurs, which ultimately leads to complete conversion of $Cu(OH)_2$ to CuS. Notwithstanding, a lower reaction rate than that in the case of metal chlorides and sulfates is to be expected.

At last but not least, it should be noted that the heavy metal oxides and hydroxides are known to be of amphoteric nature, which means that their solubility increases with an increase in pH owing to the formation of soluble cuprites, zincates, plumbates etc. By contrast, the solubility of metal sulfides decreases with an increase in pH [87,88]. Thus, an increase in the reaction rate as well as in the conversion is supposed to occur at an alkaline pH range.

1.6.4 Flotation

After the sulfidation treatment, the heavy metals can be separated from treated plating sludges or molten incineration fly ashes using flotation technique together with mineral ores of heavy metals. Taggart stressed that the flotation is the most modern, the most efficient, the most widely applicable, and in many respects the most complex of all methods of concentration [22]. Generally, flotation is based on highly specific attachment of particles of one desirable mineral or group of minerals, suspended in a solution containing various flotation additives, to air bubbles. Consequently, the bubbles (with mineral particles attached) are brought to the surface and collected to achieve separation of desirable mineral from tailings [21-23].

Presently, using the flotation technique, a sequential separation of lead, zinc, copper and iron sulfides from residual non-metallic tailings can be accomplished. **Figure 1.8** shows a typical flow sheet for polymetallic ore flotation [90]. From this figure, it can be seen that the treated plating sludge or molten incineration fly ash could be subjected as a feed to the separation process by means of flotation together with metallic ores.

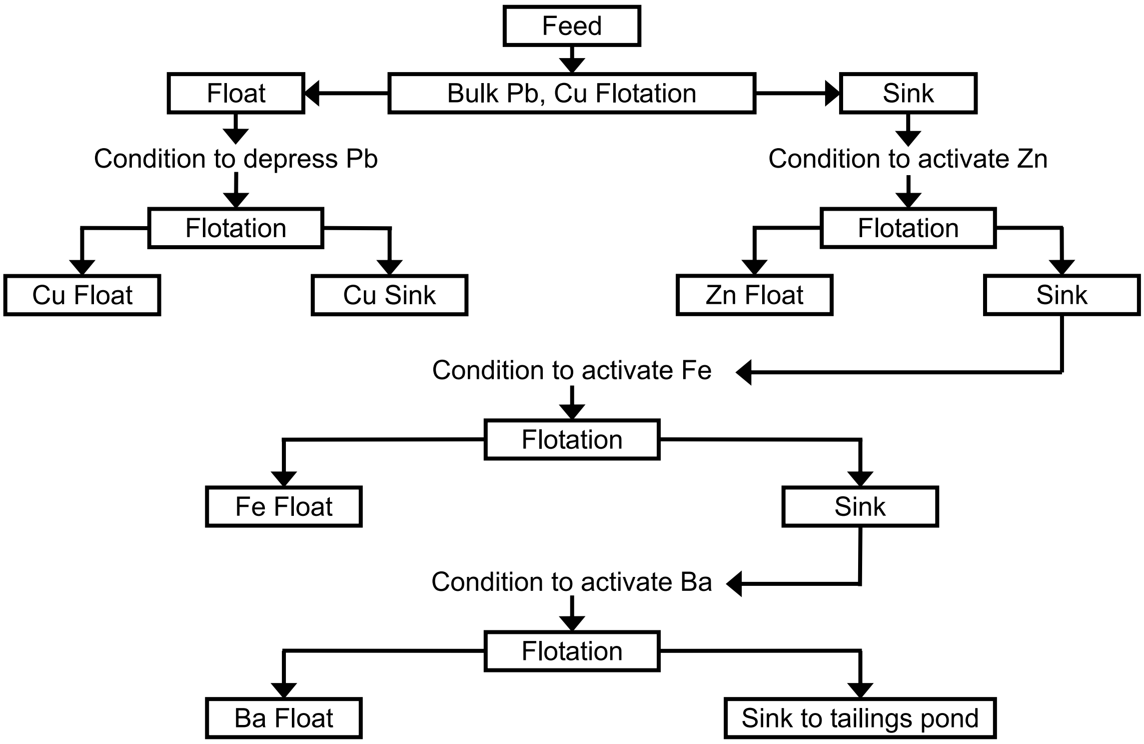


Fig. 1.8: Typical flow sheet for polymetallic ore flotation [90]

1.7 Objectives and scope of the dissertation thesis

The research presented in this dissertation work addresses the recovery of heavy metals from industrial solid wastes such as plating sludge and molten incineration fly ashes. In these types of waste, heavy metals are present in various chemical forms, and thus the conversion of heavy metals to a single chemical form allowing subsequent separation of heavy metals is required. From this point of view, the conversion to metal sulfides seems to be the best option since the metal ores are generally composed of metal sulfides. After the sulfidation treatment, the treated plating sludges and molten incineration fly ashes could be directly subjected to the flotation and subsequent metal refining process at smelters alone or together with mineral ores. In this work, the sulfidation behaviour of metal reagents such as $Cu(OH)_2$, ZnO and $Ni(OH)_2$, copper and zinc simulated plating sludges, real plating sludges and molten incineration fly ashes was investigated. And more precisely, the effects of sulfidation time, solid to liquid ratio, sulfide to metal molar ratio and pH on the conversion of metal compounds to metal sulfides were studied.

This dissertation thesis can be divided into two main parts; the first part summarizes the results of study carried out on the sulfidation treatment of plating sludges, while the second part provides the result obtained for sulfidation treatment of molten incineration fly ashes. The sulfidation treatment of plating sludges is further divided into three chapters which deal with the sulfidation treatment of metal reagents (Chapter 2), simulated plating sludges and real plating sludges (Chapters 3 and 4). The sulfidation treatment of molten incineration fly ashes is divided into a fundamental study on sulfidation of fly ash from municipal or industrial waste incineration process (Chapter 5) and a more detailed study on sulfidation behaviour of molten incineration fly ashes (Chapter 6).

<u>Brief summary of each chapter is given as follows:</u>

Chapter 2 focuses on the sulfidation behaviour of metal reagents of $Cu(OH)_2$, ZnO and $Ni(OH)_2$. In this chapter, the effects of reacting time, solid to liquid ratio and pH on the conversion of these metal compounds to metal sulfides were studied. Further, the formation of sulfidation products was analyzed using X-ray powder diffraction (XRD).

Chapter 3 presents the results on the sulfidation treatment of simulated copper plating sludge and real copper plating sludge. More precisely, the effect of the S^{2-} to Cu^{2+} molar ratio (S^{2-} to Me^{2+} molar ratio in the case of real plating sludge) on the formation of copper sulfide was investigated. The formation of various copper sulfides observed in this study was explained in terms of oxidation-reduction potential and Eh-pH diagram.

Chapter 4 aims at investigating the sulfidation treatment of simulated zinc plating sludge and the effects of time, pH and solid to liquid ratio on the conversion of zinc compounds to ZnS. Further, an attempt was made to describe the conversion using Elovich kinetics model. Finally, the validity of the results obtained with simulated zinc plating sludge was verified using a real sludge with high content of zinc.

Chapters 5 deals with the sulfidation treatment of two molten incineration fly ashes; molten incineration fly ash from municipal solid waste incinerator and automobile shredder residue incinerator. In particular, the effects of treating time and S^{2-} to Me^{2+} molar ratio on the conversion were investigated.

Chapter 6 provides the results of a more elaborated study on the sulfidation behaviour of molten incineration fly ashes and the experiments in this chapter were carried out for five different molten incineration fly ashes. Particularly, the effects of treating time, S^{2-} to Me^{2+} molar ratio and pH on the conversion were thoroughly investigated. The formation of metal sulfides was confirmed using X-Ray powder diffraction (XRD) and scanning electron microscopy – energy dispersive spectrometry (SEM-EDS). In addition, the enrichment of heavy metals during sulfidation treatment as a result of the removal of soluble salts was evaluated using an enrichment factor.

Finally, Chapter 7 summarizes the results of this dissertation thesis and also gives some suggestions for future research work.

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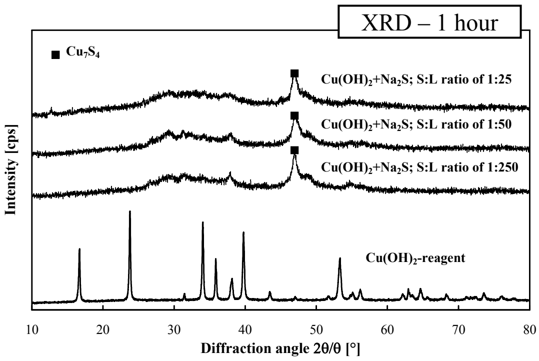
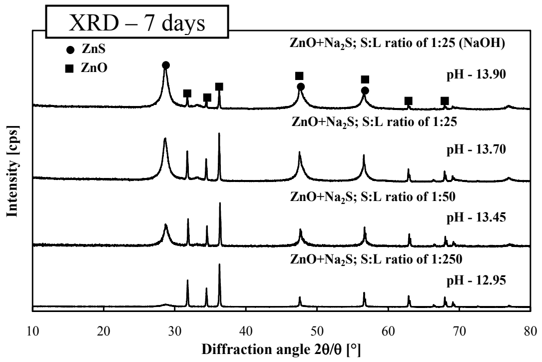
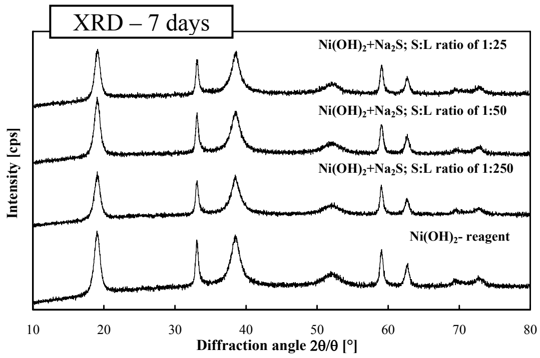
CHAPTER 2

Fundamental study on the sulfidation of metal compounds involved in plating sludges







This chapter presents the results of sulfidation treatment conducted separately for metal reagents of $Cu(OH)_2$, ZnO or $Ni(OH)_2$. As a sulfidation agent, Na_2S solution was used. The XRD results showed that $Cu(OH)_2$ was completely converted to copper sulfides within 1 hour at all S:L ratios. In the case of ZnO, the formation of ZnS was confirmed by XRD, but the conversion of ZnO to ZnS was found to be strongly dependent on S:L ratio as well as on the pH value. The maximum conversion of ZnO to ZnS of 60.3% was obtained after 7 days at S:L ratio of 1:25 (pH of 13.7). Finally, the maximum conversion of $Ni(OH)_2$ to nickel sulfides was determined by means of TG analysis to be only 32.4% after 7 days at the S:L ratio of 1:25, but the formation of nickel sulfides was not confirmed by XRD analysis.

2.1 Introduction

In Japan, heavy metals such as copper, zinc, nickel and chromium in the form of their metallic salts are used in the plating industry. Generally, these metals are deposited on the surface of the products being plated, but during rinsing of the plated products, a part of heavy metals-plating solution is washed out and discharged as a rinsing wastewater. The rinsing wastewater contains soluble metallic salts such as $ZnSO_4$, $CuSO_4$, and $NiSO_4$ at high concentrations of about 100-300 mg/L. In the treatment of rinsing wastewater, the concentration of heavy metals has to be decreased to values below the permissible limits [1]. In Japan, the permissible limits for wastewater discharge from electroplating industry are 3 mg/L and 5 mg/L for Cu and Zn, respectively [2]. To remove the heavy metals from rinsing wastewater, and thus, to meet the permissible limits, chemical precipitation with either NaOH or $Ca(OH)_2$ is used and the pH of the rinsing wastewater is adjusted to a value in the range of 9.2 to 9.5. The precipitation is allowed to proceed for at least 15 minutes [1,3] and the precipitate/plating sludge arising thereof is separated by coagulation, sedimentation and filtration processes. The plating sludge is then disposed and appropriate measures have to be taken to ensure the long-term stability at the site location [4]. For this purpose, plating sludge is treated with a stable binding material, such as cement, lime, fly ash [5-7] or asphalt emulsion [8], while further solidification pre-treatment, such as conversion of metals to sulfides or silicates can be employed [9].

Currently, as a result of the treatment described above, the valuable metals are rather disposed of to landfill than subjected to the process of heavy metals recovery. It results from the fact that the heavy metals are present in the sludge in various chemical forms such as metal hydroxides [1] or metal hydroxide sulfates [10] as well as from the presence of inorganic salts [11]. Therefore, in order to recover heavy metals, the conversion of heavy metals to a uniform chemical form is required. In this work, the conversion of heavy metals to metal sulfides is proposed since the heavy metal sulfides can be separated by means of the flotation technique, a commonly used separation technique for sulfide ores [12-14]. After the sulfidation treatment, the treated sludge could be directly subjected to the metal refining process.

In this chapter, the sulfidation treatment was carried out using the metal reagent of $Cu(OH)_2$, ZnO or $Ni(OH)_2$, typically involved in plating sludge, in order to investigate the conversion characteristics of these metals to metal sulfides. To achieve the conversion of $Cu(OH)_2$, ZnO and $Ni(OH)_2$ to metal sulfides, the metal reagents were separately contacted with Na_2S aqueous solution for a period varying from 1 hour to 7 days, and the effects of solid to liquid (S:L) ratio, sulfidation time and pH of the reacting systems on the conversion were investigated. The evaluation of conversion was based on thermogravimetric analysis as well as on X-ray powder diffraction analysis of the dried sulfidation products.

2.2 Experimental part

2.2.1 Materials

Copper hydroxide and nickel hydroxide of reagent grade (Wako Pure Chemical Industries, Ltd.) were employed in this study since the metal hydroxides are typically present in plating sludges. In the case of zinc which is also present in plating sludge in the hydroxide form, zinc oxide of reagent grade (Wako Pure Chemical Industries, Ltd.) was used for the experiments because of unavailability of $Zn(OH)_2$. The solid ZnO dissolves in water according to Eq. (2.1) [15].

$$ZnO(s) + H_2O \leftrightharpoons Zn^{2+} + 2OH^- \tag{2.1}$$

As a sulfidation agent, $Na_2S{\cdot}9H_2O$ of reagent grade (Wako Pure Chemical Industries, Ltd.) was employed.

2.2.2 Treatment procedure

The sulfidation treatment of metal reagents was performed in a batch system, and the experimental procedure is described as follows. At first, a volume of 50 mL or 250 mL aqueous Na_2S solution, prepared in advance, was poured into a plastic container, while the amount of $Na_2S{\cdot}9H_2O$ dissolved in distilled water was such that an initial molar ratio of S^{2-} to Me^{2+} was adjusted to 1.5. Second, an appropriate amount of $Cu(OH)_2$, $Ni(OH)_2$ or ZnO was charged into each container to achieve a solid to liquid (S:L) ratio of 1:250 (weight concentration of about 4 g/L), 1:50 (weight concentration of about 20 g/L) or 1:25 (weight concentration of about 40 g/L). Third, the plastic containers were shaken on a vertical shaker for a period of 1 hour to 7 days, and finally, the slurry was filtered using a 1 μm pore size filter paper.

2.2.3 Analyses of filtrates and filter cakes

The filter cake was dried for 2 days at an ambient temperature of about 25°C, and then subjected to thermogravimetric (TG) analysis (TGA-50, Shimadzu Corporation, Japan) which was carried out under N_2-O_2 atmosphere at a ratio of 4:1, gas flow rate of 50 mL/min and a temperature increase of 2°C/min. Furthermore, the dried filter cake was subjected to X-Ray powder diffraction (XRD) analysis (RINT-2500 TTR, Rigaku Model, Japan) with scanning mode of 2θ/θ. The filtrates were subjected to the determination of heavy metals using inductively coupled plasma (ICP) equipment (Vista-MPX Simultaneous ICP-OES, Varian, Inc.).

2.3 Results and discussion

The plating sludges are composed of metal hydroxides which are characterized by low solubility product constants. Hence, only limited amounts of metal ions arising from dissolution are present in solution and the bulk part of metal hydroxides remains un-dissolved. However, if the free metal ions are continuously removed from solution by precipitation with S^{2-} ions, the dissolution of metal hydroxide is allowed to proceed, due to a shift in equilibrium position, which ultimately leads to a complete conversion of metal hydroxides to metal sulfides. The reaction mechanism is shown in Eqs. (2.2)-(2.3) where Me^{2+} stands for Cu^{2+}, Zn^{2+} or Ni^{2+} cation.

$$Me(OH)_2(s) \leftrightharpoons Me^{2+} + 2OH^- \tag{2.2}$$

$$Me^{2+} + S^{2-} \leftrightharpoons MeS(s) \tag{2.3}$$

2.3.1 Conversion of $Cu(OH)_2$ to CuS

2.3.1.1 Effect of time on conversion of $Cu(OH)_2$ to copper sulfide

The effect of time on the conversion of $Cu(OH)_2$ to copper sulfide was investigated for a time period varying from 1 hour to 7 days at a S:L ratio of 1:50, while the initial molar ratio of S^{2-} to Cu^{2+} was adjusted to a value of 1.5. The evaluation of conversion of copper hydroxide to copper sulfide was based on XRD analyses and the XRD patterns obtained are shown in **Fig. 2.1**. It was found that $Cu(OH)_2$ was readily converted to a copper sulfide, namely Cu_7S_4 (roxbyite), within 1 hour. Moreover, other copper sulfides such as Cu_2S, Cu_8S_5, $Cu_{31}S_{16}$ with the molar ratio of copper to sulfur of approximately 2 to 1 where identified in the sulfidation products at diffraction angle range of 47 to 49 degrees.

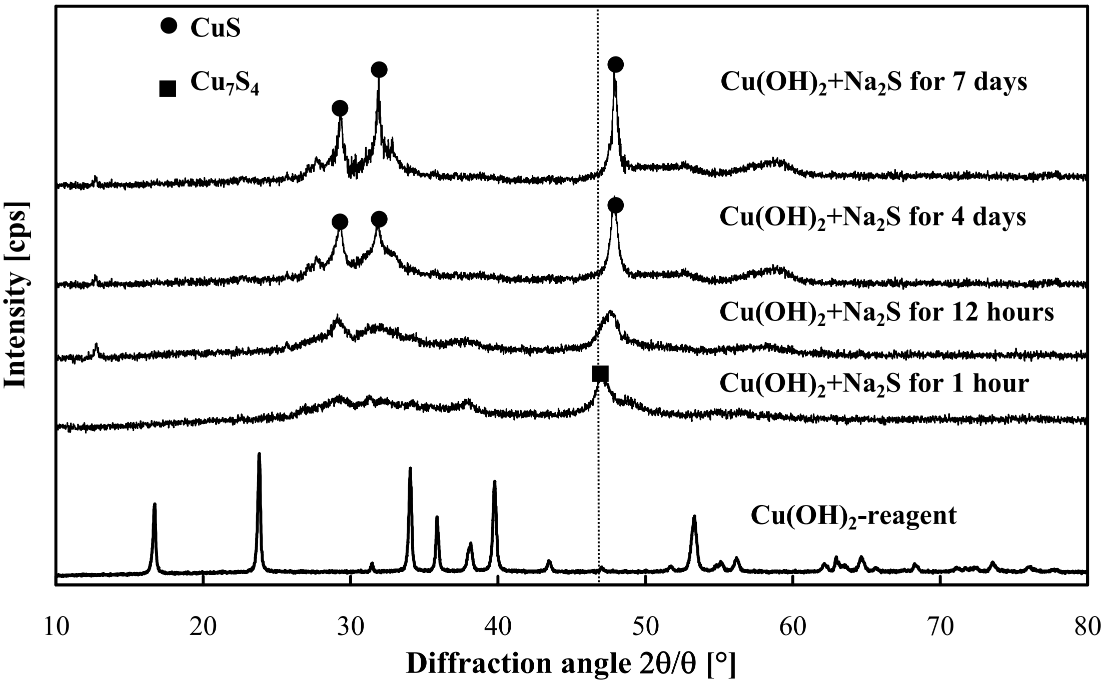


Fig. 2.1: Effect of time on XRD patterns of $Cu(OH)_2$ treated with Na_2S at S:L ratio of 1:50

Given the preceding observations, it was concluded that the general reaction mechanism shown in Eq. (2.3) did not hold for the conversion of $Cu(OH)_2$ to CuS, and a new reaction mechanism obtained from chemical reaction and equilibrium software

(HSC Chemistry Ver.3.02) was proposed, as shown in Eqs. (2.4) and (2.5). It is also considered that a similar reaction mechanism could be applied to the formation of Cu_7S_4, Cu_8S_5, $Cu_{31}S_{16}$ identified in the sulfidation products, since these sulfides have the molar ratio of copper to sulfur of about 2 to 1.

$$2Cu^{2+} + 2S^{2-} \rightleftharpoons 2Cu^{+} + S_2^{2-} \qquad \Delta G(298K)= -123.1\ kJ/mol \qquad (2.4)$$

$$2Cu^{+} + S^{2-} \rightleftharpoons Cu_2S \qquad \Delta G(298K)= -272.4\ kJ/mol \qquad (2.5)$$

$$2Cu^{2+} + 3S^{2-} \rightleftharpoons Cu_2S(s) + S_2^{2-} \qquad \Delta G(298K)= -395.5\ kJ/mol \qquad (2.6)$$

The Eq. (2.6) represents the overall reaction consisting of the oxidation-reduction reaction of Cu^{2+} (reduced to Cu^{+}) with S^{2-} (oxidized to S_2^{2-}) as shown in Eq. (2.4) and the following precipitation reaction of Cu^{+} with S^{2-} (Eq. (2.5)). The overall Gibbs free energy of -395.5 kJ/mol calculated using HSC Chemistry Ver.3.02 was almost twice greater than the Gibbs free energy for the reaction given by Eq. (2.3), which suggests that the reaction given by Eq. (2.6) should proceed preferentially. When the treatment period was further extended up to 7 days a gradual conversion of Cu_7S_4 to CuS (covellite) was observed, but the exact reaction mechanism remained unclear.

To confirm the conversion of $Cu(OH)_2$ to copper sulfides (Cu_xS_y), a sulfidation product obtained by contacting $Cu(OH)_2$ with Na_2S for 1 hour at the S:L ratio of 1:50 was subjected to TG analysis and the results are shown in **Fig. 2.2**. It can be seen that the reagent of $Cu(OH)_2$ decomposed to CuO at a temperature of about 145°C. By contrast, no significant weight loss was observed when $Cu(OH)_2$ was treated with Na_2S for 1 hour, which confirmed the conversion of copper hydroxide to Cu_xS_y. When the sulfidation product was further heated, a partial oxidation of Cu_xS_y to $CuSO_4$ occurred at the temperature above 250°C. Finally, copper sulfate decomposed to copper oxide at a temperature of about 650°C [16].

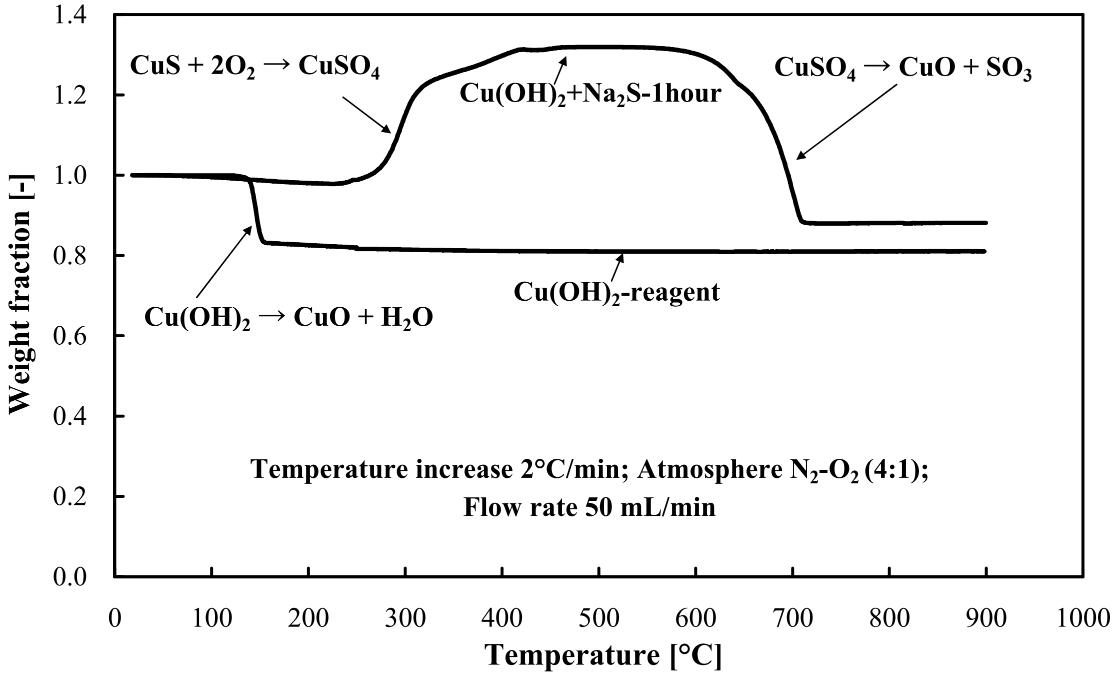


Fig. 2.2: TG analysis of $Cu(OH)_2$ and $Cu(OH)_2$ treated with Na_2S at S:L ratio of 1:50 for 1 hour

2.3.1.2 Effect of S:L ratio on conversion of $Cu(OH)_2$ to copper sulfide

The content of copper compounds, as well as the content of zinc and nickel compounds usually varies from sludge to sludge, and therefore it was necessary to find a range of S:L ratio suitable for the conversion of copper hydroxide to copper sulfide. Besides, an amount of $Na_2S{\cdot}9H_2O$ dissolved in water to establish given S^{2-} to Cu^{2+} initial ratio of 1.5 for each S:L ratio significantly affected pH value of the reacting system. Hence, the evaluation of the effect of S:L ratio on conversion of $Cu(OH)_2$ to copper sulfide was necessary and was carried out by contacting $Cu(OH)_2$ with Na_2S solution for 1 hour at S:L ratios of 1:250 and 1:25. In these experiments, the pH value increased from 12.8 for S:L ratio of 1:250 to 13.6 for S:L ratio of 1:25. **Figure 2.3** shows the XRD patterns of the sulfidation products obtained at different S:L ratios and it was confirmed that the conversion of $Cu(OH)_2$ to copper sulfide could be successfully carried out in a wide range of S:L ratio.

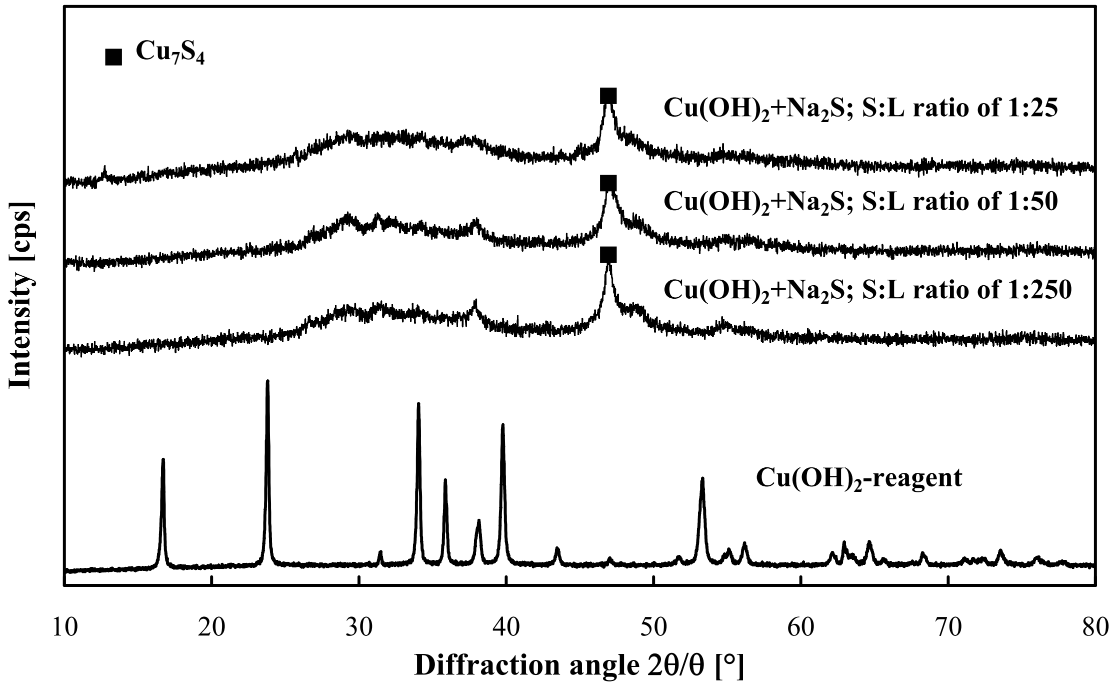


Fig. 2.3: XRD patterns of $Cu(OH)_2$ treated with Na_2S for 1 hour at different S:L ratios

In addition to the above, a determination of copper in filtrates obtained by filtration of the slurry using a 1 μm pore size filter paper was performed and it was found that the concentrations of copper in filtrate were lower than 5 mg/L.

2.3.2 Conversion of ZnO to ZnS

2.3.2.1 Effect of S:L ratio on the conversion of ZnO to ZnS

The conversion of ZnO to ZnS was studied for a period of 1 hour to 7 days at S:L ratios of 1:25, 1:50 and 1:250, and the initial molar ratio of S^{2-} to Zn^{2+} was set at 1.5. The conversion of ZnO to ZnS was determined using TG analysis, as shown in **Fig. 2.4**. When ZnS was heated above 550°C under N_2-O_2 atmosphere, ZnS was oxidized to ZnO, which was accompanied by a weight loss owing to the lower molecular weight of ZnO. A complete conversion of ZnS to ZnO was achieved at a temperature of 900°C. In the case of ZnO treated with Na_2S, a partial oxidation of ZnS, formed during the sulfidation treatment, to $ZnSO_4$ was observed when the sample was heated beyond 260°C. Then, the $ZnSO_4$ formed was decomposed to ZnO at a temperature of about 780°C. Besides, it was observed that the conversion of ZnS to ZnO started at a lower temperature of about 500°C compared to that of ZnS reagent. It is considered that both the oxidation of ZnS to $ZnSO_4$ and conversion of ZnS to ZnO at a lower temperature resulted from irregularities in crystal lattice of ZnS formed by sulfidation treatment of ZnO. Consequently, the irregular crystals were more susceptible to oxidation and decomposition than those of ZnS reagent.

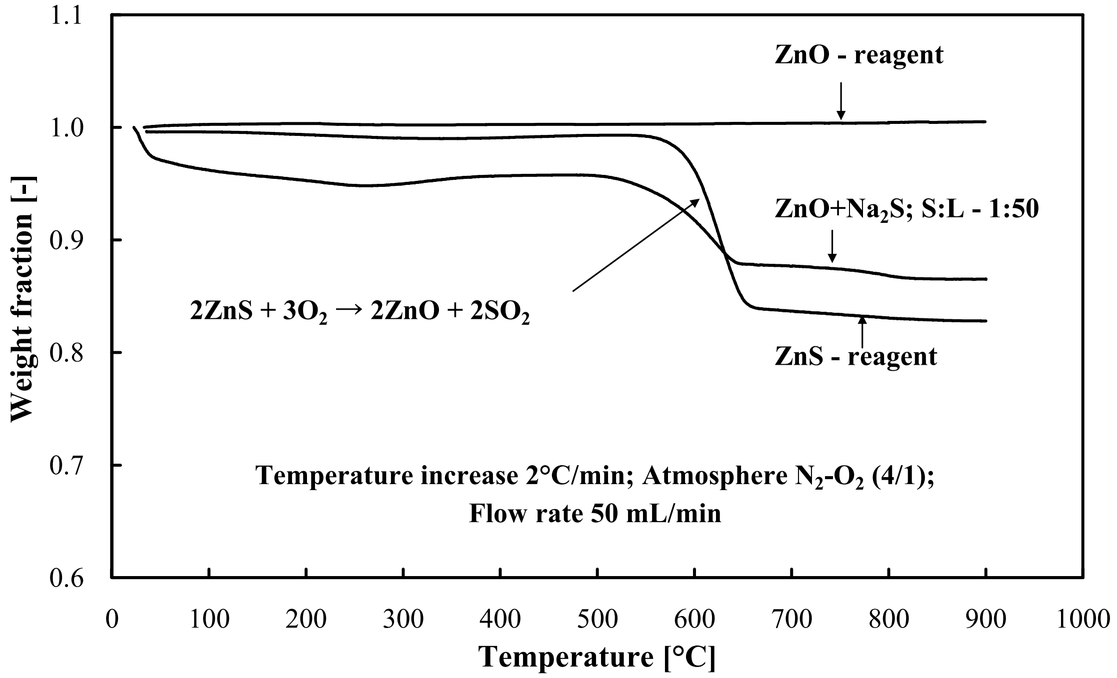


Fig. 2.4: TG analysis of ZnO, ZnS, and ZnO treated with Na_2S for 7 days at S:L ratio of 1:50

In **Fig. 2.5**, the conversion of ZnO to ZnS derived from TG analyses is plotted against time for different S:L ratios. It was found that conversion increased with an increase in S:L ratio, and the conversion values obtained after 7 days were 21.5%, 44.1% and 60.3% for S:L ratios of 1:250, 1:50 and 1:25, respectively. This increase was partially attributed to an increase in pH value owing to higher amounts of $Na_2S \cdot 9H_2O$ dissolved in water to establish the initial molar ratio of S^{2-} to Zn^{2+} of 1.5. The pH values of the reacting systems for each S:L ratio are also indicated in **Fig. 2.5**.

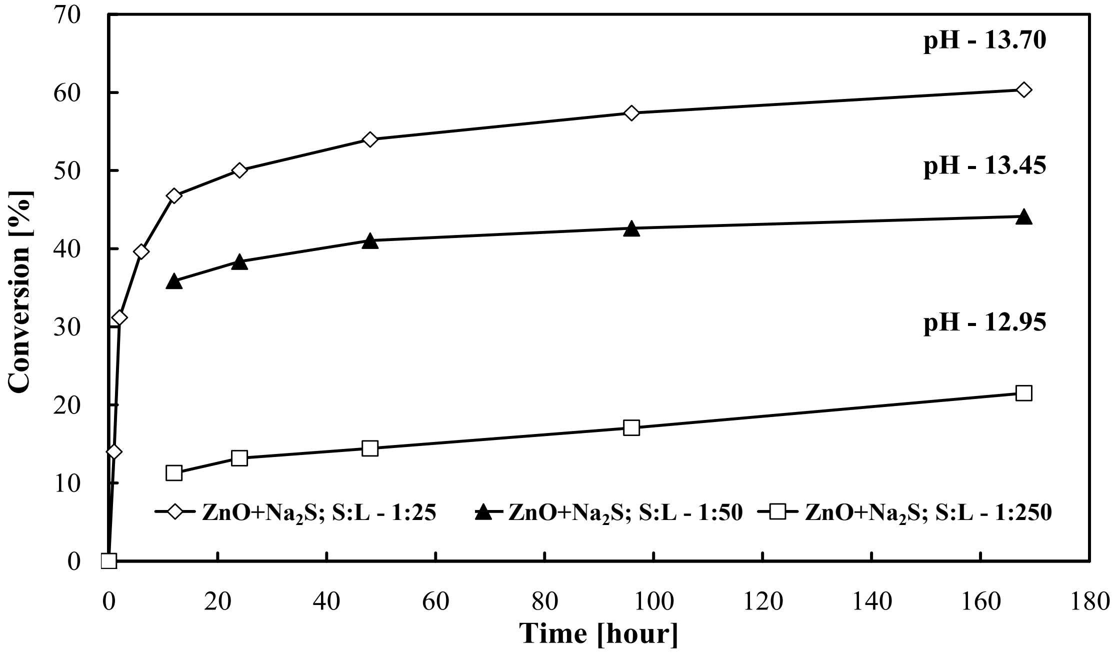


Fig. 2.5: Conversion of ZnO to ZnS

The significance of pH arose from an increase in solubility of ZnO with an increase in pH owing to the formation of more soluble zincates according to Eqs. (2.7) and (2.8) [15].

$$Zn^{2+} + 3OH^- \leftrightharpoons Zn(OH)_3^- \quad (2.7)$$

$$Zn^{2+} + 4OH^- \leftrightharpoons Zn(OH)_4^{2-} \quad (2.8)$$

It is therefore postulated that solubility of ZnO was a controlling factor of the extent and rate of conversion of ZnO to ZnS, while the precipitation of ZnS (Eq. (2.9)-(2.11)) was supposedly instantaneous, since the concentrations of Zn measured in the filtrates were less than 1 mg/L.

$$Zn^{2+} + S^{2-} \leftrightharpoons ZnS(s) \quad (2.9)$$

$$Zn(OH)_3^- + S^{2-} \leftrightharpoons ZnS(s) + 3OH^- \quad (2.10)$$

$$Zn(OH)_4^{2-} + S^{2-} \leftrightharpoons ZnS(s) + 4OH^- \quad (2.11)$$

In order to further increase the conversion ratio, ZnO at an amount corresponding to S:L ratio of 1:25 was contacted with Na_2S solution prepared by dissolving $Na_2S{\cdot}9H_2O$ in 1M NaOH of which the pH value was 13.9. Interestingly, it was found that the conversion ratio achieved after 7 days was only 51.3%. It was hypothesized that at a high pH value, ZnS could have been precipitated on the surface of ZnO particles, which led to an enclosure of ZnO, and thus, the complete conversion of ZnO to ZnS was prevented.

To confirm the formation of ZnS, dried sulfidation products were subjected to XRD analyses and the XRD patterns are depicted in **Fig 2.6**. A relative increase in intensity of characteristic peaks of ZnS compared to those of ZnO was observed when pH was increased from 12.95 to 13.7, which confirmed the results obtained using TG analysis (**Fig. 2.5**). By contrast to the results of TG analysis for ZnO shaken at pH of about 13.9, the characteristic peaks of ZnS were remarkably higher compared to those of ZnO, but the conversion ratio achieved was only 51.3%. It seems to confirm that unreacted ZnO was enclosed in ZnS particles formed.

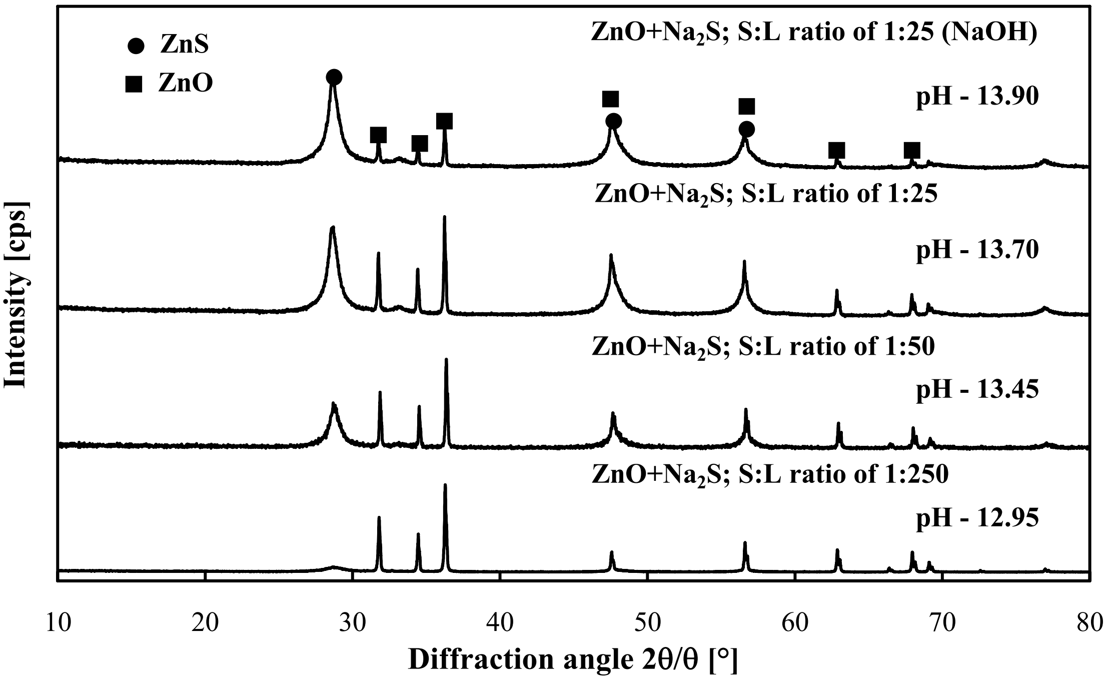


Fig. 2.6: XRD patterns of ZnO treated with Na_2S for 7 days at different S:L ratios

2.3.2.2 Effect of pH of the reacting system on conversion of ZnO to ZnS

As described in the previous section, the conversion of ZnO to ZnS was significantly affected by changes in S:L ratio, which were also accompanied by changes in pH of the reacting systems. Therefore, the effect of pH of the reacting system on conversion of ZnO to ZnS was further investigated at the S:L ratio of 1:250 and treatment period of 7 days. The pH value of the reacting system was varied by dissolving $Na_2S{\cdot}9H_2O$ in distilled water with 1M NaOH additions of 20, 50, 100, or 150 mL to make up the total volume to 250 mL. The conversion results obtained are shown in **Fig. 2.7** and it was confirmed that the conversion strongly depended on pH value owing to a higher solubility of ZnO.

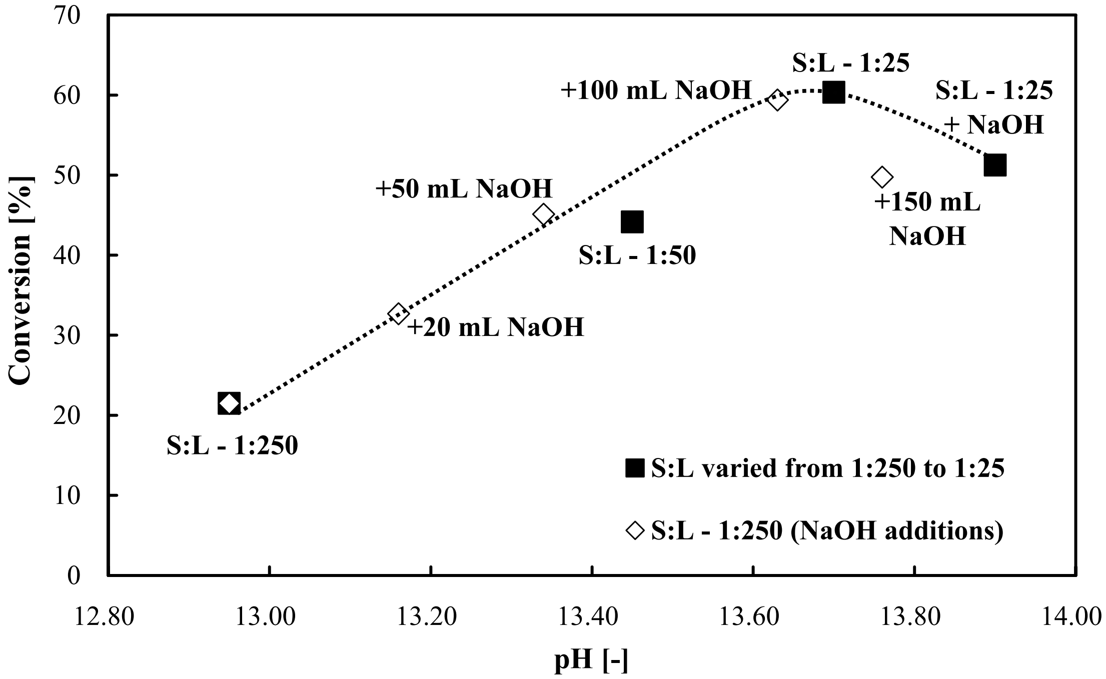


Fig. 2.7: Conversions of ZnO to ZnS obtained after 7 days treatment at different pH value of reacting system

The maximum conversion was 59.4%, obtained at a pH value of 13.6. When the pH value of the reacting system was further increased, the conversion was reduced to only 49.7%, which corresponded to the previously obtained results at S:L ratio of 1:25. Given the preceding observations, it is inferred that at a pH value above 13.7, ZnO started to rapidly dissolve into the Na_2S solution and Zn^{2+} ions were instantaneously precipitated with S^{2-} forming a thin and almost monolithic layer on ZnO particles. The subsequent dissolution of ZnO was thus prevented leading to a lower conversion.

2.3.3 Conversion of $Ni(OH)_2$ to NiS

The investigation on conversion characteristics of $Ni(OH)_2$ was performed by contacting $Ni(OH)_2$ with Na_2S solution for 7 days at S:L ratio varying from 1:250 to 1:25. The sulfidation products were analyzed using XRD and the XRD patterns obtained are shown in **Fig. 2.8**. It can be seen that the sulfidation products were composed of $Ni(OH)_2$ and no peaks of nickel sulfide were identified.

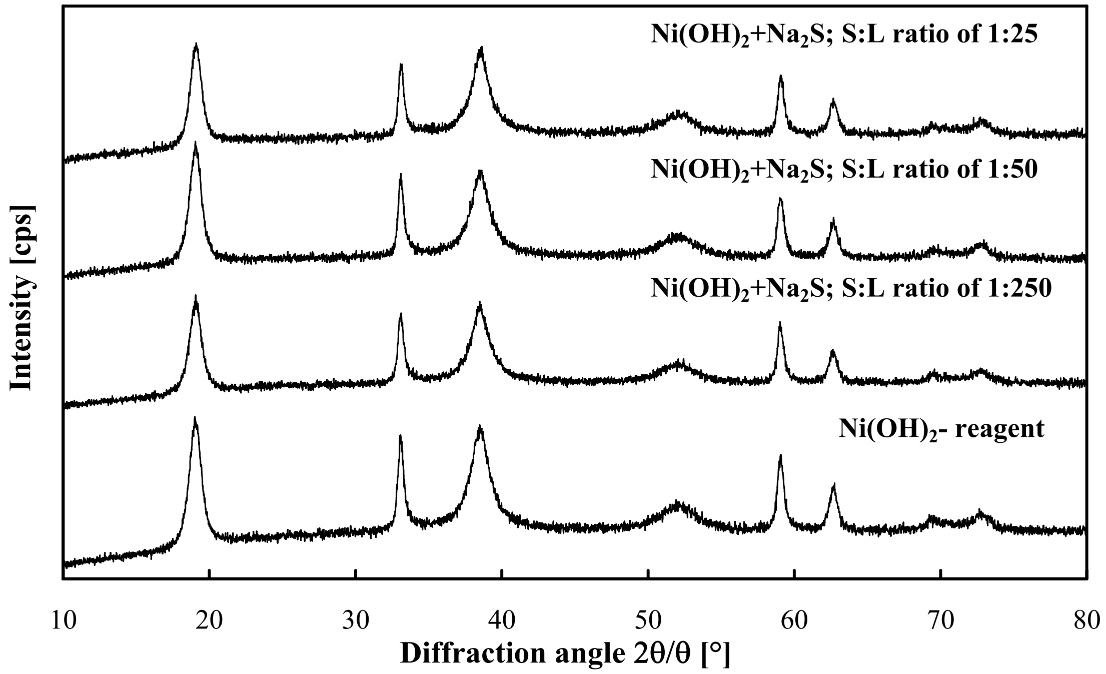


Fig. 2.8: XRD patterns of $Ni(OH)_2$ treated with Na_2S for 7 days at different S:L ratios

These results suggest that the reagent of $Ni(OH)_2$ remained unconverted, and thus, to further analyze the sulfidation products, the samples were subjected to TG analysis. The TG analysis showed two significant weight losses at the temperatures of about 230°C and 690°C. The first weight loss corresponded to the decomposition of residual $Ni(OH)_2$ to NiO, while the second weight loss was attributed to the conversion of nickel sulfides to NiO. Since the nickel sulfide was not identified using XRD analyses, and moreover the molar ratio of Ni^{2+} to S^{2-} in sulfidation products remained unknown, the determination of conversion of $Ni(OH)_2$ to nickel sulfide was based on the determination of residual $Ni(OH)_2$.

As a result, it was found that only 17.5% of $Ni(OH)_2$ was converted to nickel sulfide after 7 days at a S:L ratio of 1:250 and the conversion increased only to 28.9% when the S:L ratio was increased to 1:25. Therefore, it was concluded that $Ni(OH)_2$ was not easily convertible to nickel sulfide when treated with Na_2S, due to the low solubility of $Ni(OH)_2$. It was reported that theoretical solubility of $Ni(OH)_2$ was only about 0.2 mg/L and about 5 mg/L at pH value of 12 and 14, respectively [17], while the solubility of nickel from plating sludge at pH value of 12.5 was about 2 mg/L [18]. Based on the solubility data and also on the fact that the highest conversion was achieved at S:L ratio of 1:25 (pH value of 13.6), the effect of pH was further investigated. The reagent of $Ni(OH)_2$ was for 7 days contacted with Na_2S solution, prepared by dissolving given amounts of $Na_2S \cdot 9H_2O$ in 1M NaOH, at the S:L ratios of 1:250, 1:50 and 1:25. However, no increase in the conversion was observed.

Besides, it was found that sulfidation treatment of $Ni(OH)_2$ brought about the formation of small particles of nickel sulfide which were not separable even by filtration using a 0.22 μm filter paper. To determine the concentration of nickel in the filtrate, an aliquot portion of each filtrate was dissolved in aqua regia, a mixture of hydrochloric acid and nitric acid, and then analyzed using ICP. The concentrations of nickel measured in the filtrates were 57 mg/L, 610 mg/L and 1 505 mg/L for S:L ratios of 1:250, 1:50 and 1:25, respectively. The nickel concentrations in the filtrate corresponded to 0.42%, 3.98% and 4.91% of the initial sample weight for S:L ratios of 1:250, 1:50 and 1:25, respectively. When the conversion was determined based on the nickel balance in the filtrate and the filter cake, the maximum conversion of 17.8%, 20.5% and 32.4% were obtained for the samples of $Ni(OH)_2$ treated for 7 days at the S:L ratios of 1:250, 1:50 and 1:25, respectively.

2.4 Conclusions

The conversion of Cu, Zn and Ni to metallic sulfides was studied by contacting separately the reagents of $Cu(OH)_2$, ZnO or $Ni(OH)_2$ with Na_2S solution at various S:L ratios for time period varying from 1 hour to 7 days. After sulfidation treatment, the samples were dried and subjected to XRD and TG analyses to evaluate the conversion of these metals to metal sulfides. The main conclusions are summarized as follows:

- It was found that $Cu(OH)_2$ was completely converted to Cu_xS_y (mainly Cu_7S_4) which had the molar ratio of copper to sulfur of about 2 to 1. The conversion was achieved within 1 hour of contacting $Cu(OH)_2$ with Na_2S solution and was irrespective of S:L ratio. When the contact period was extended up to 7 days (S:L ratio of 1:50), a gradual conversion of Cu_7S_4 to CuS (covellite) was observed.

- The conversion of ZnO to ZnS was found to be strongly dependent on pH of the reacting system, which resulted from an increase in solubility of ZnO at higher pH values owing to the formation of more soluble zincates. The conversion ratio of ZnO to ZnS increased from 21.5% at pH value of 12.95 (S:L ratio of 1:250) to 60.3% at pH value of 13.7 (S:L ratio of 1:25), after 7 days. Interestingly, when the pH value of the reacting system was further increased by using 1M NaOH, and ZnO was treated with Na_2S at S:L ratio of 1:25, the conversion obtained after 7 days was only 51.3%. It is considered that at a pH value above 13.7, ZnO started to rapidly dissolve into the Na_2S solution and Zn^{2+} ions were instantaneously precipitated with S^{2-} forming a thin and almost monolithic layer on ZnO particles. The subsequent dissolution of ZnO was thus prevented leading to a lower conversion.

- The conversion ratio of $Ni(OH)_2$ to nickel sulfide was kept at a low value of about 17.8% for a S:L ratio of 1:250 and increased to only 32.4% when $Ni(OH)_2$ was treated for 7 days at a S:L ratio of 1:25. It is considered that a relatively low conversion of $Ni(OH)_2$ to nickel sulfide resulted from a low solubility of $Ni(OH)_2$ at high pH values.

- Finally, based on the results separately obtained for the metal reagents of $Cu(OH)_2$, ZnO or $Ni(OH)_2$, the sulfidation treatment of real plating sludges was proposed.

In particular, it is considered that a real plating sludge could be treated with Na_2S in order to convert heavy metals to metal sulfides. Subsequently, the metal sulfides formed could be selectively recovered by means of flotation technique, as shown in **Fig. 2.9**. In the flotation process shown, the separation of copper sulfide is achieved in the first step, followed by zinc sulfide separation in the second step; however further investigation to increase the conversion of zinc compounds to zinc sulfide is essential. Finally, the flotation residue composed mainly of nickel compounds could be treated to recover nickel resource.

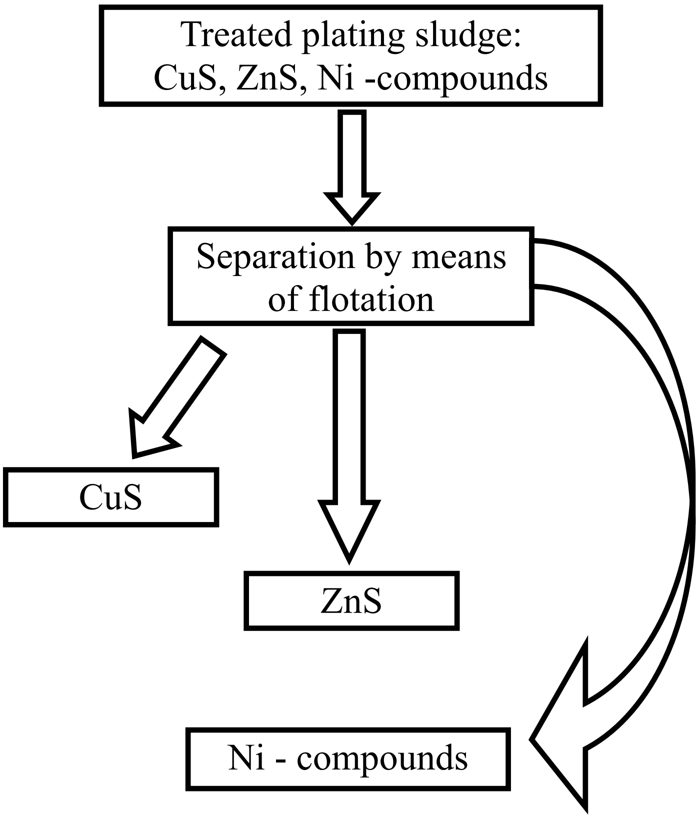


Fig. 2.9: Proposed separation procedure of plating sludge treated with Na_2S

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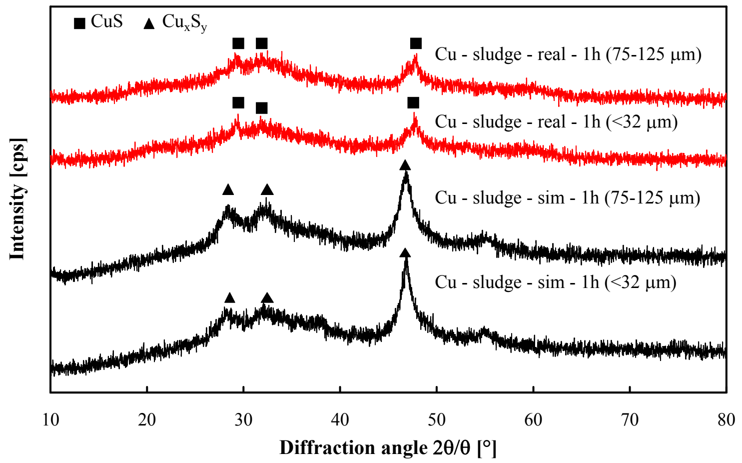
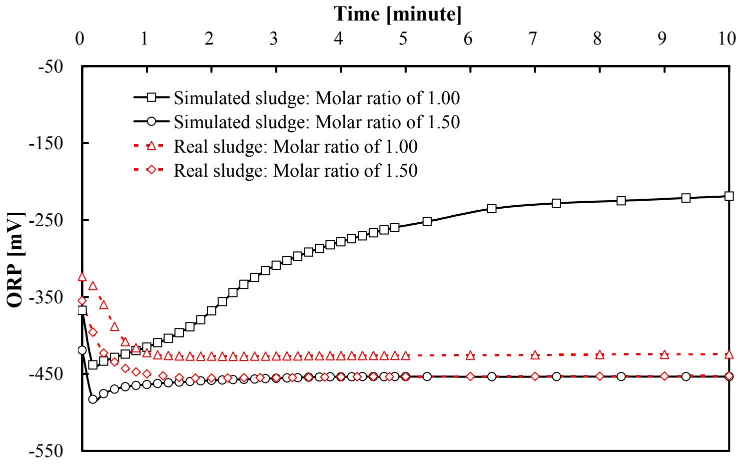
CHAPTER 3

Sulfidation treatment of copper plating sludges





In this chapter, the sulfidation treatment with Na_2S solution was separately carried out for simulated and real copper plating sludge in order to confirm the results obtained for $Cu(OH)_2$. Similarly to $Cu(OH)_2$, copper compounds were converted to various copper sulfides within the first 5 minutes. The XRD analyses of the sulfidation products showed that in the case of real copper sludge and simulated copper sludge (S^{2-} to Cu^{2+} molar ratio of 1.00), CuS was the main sulfidation product. By contrast, Cu_7S_4 (Roxbyite) was mainly found in the case of simulated copper sludge at the molar ratios of S^{2-} to Cu^{2+} of 1.50 and 1.25. The formation of different copper sulfides was explained using ORP measurements and Eh-pH diagram.

3.1 Introduction

Electroplating is a technique used for surface finishing of metals, ceramics and plastics. In Japan, heavy metals such as zinc, copper, nickel, chromium and tin are commonly used by electroplating and copper accounts for about 30% (5,732 tons/year) of the total amount of metals consumed [1]. In Chapter 2, the sulfidation treatment was carried out for metal reagent of $Cu(OH)_2$ and it was found that copper hydroxide can be easily converted to various copper sulfides. Thus, in the next step, the sulfidation treatment was conducted for simulated and real copper plating sludge in order to confirm the results obtained for $Cu(OH)_2$. Similarly as in Chapter 2, Na_2S aqueous solution was used as a sulfidation agent, and the initial molar ratio of S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} in the case of real plating sludge) was adjusted to 1.00, 1.25 or 1.50. The solid to liquid (S:L) ratio was fixed at 1.00:50 (1.00 g sludge to 50 mL Na_2S solution). The S:L ratio of 1:50 was chosen with respect to the results presented in Chapter 2, where the effect of S:L ratio on the conversion was investigated for copper hydroxide in the range of S:L ratio of 1:250 to 1:25 and it was found that, in this range, the conversion of copper hydroxide to copper sulfide was not affected by the S:L ratio. The residual amount of sulfide ions remaining in the solution after contacting the simulated or real copper plating sludge with Na_2S solution for a period of 5 minutes to 24 hours was analyzed using an ion selective electrode. Further, the sulfidation products were identified by means of an XRD analysis and the formation of various copper sulfides was explained using Eh-pH diagram. Finally, the effect of particle size on the conversion was studied in the particle size range of 0 to 125 μm.

3.2 Experimental part

3.2.1 Preparation of copper plating sludge

3.2.1.1 Simulated copper plating sludge

The simulated copper plating sludge was prepared according to flow chart shown in **Fig. 3.1(a)**. An amount of 12.8 g $CuSO_4 \cdot 5H_2O$ of reagent grade (Wako Pure Chemical Industries, Ltd.) was dissolved in a 400 mL distilled water. Then, the pH value of the solution was increased from about 4.20 to 9.40±0.1 using 1M NaOH solution, under continuous stirring, to make up a total volume of about 500 mL. As a consequence of the increase in pH, copper ions were precipitated as insoluble copper hydroxide and copper hydroxide sulfates such as posnjakite and brochantite [2,3]. The precipitation was allowed to proceed for 30 minutes and then the slurry/precipitate formed was filtered using a filter paper with pore size of 1 μm. The precipitate was, then, rinsed in 500 mL distilled water for another 30 minutes, in order to purify the copper precipitate. During rinsing, the pH value was kept constant at the value of 9.40±0.1. In the subsequent step, the precipitate was again filtered using a filter paper with pore size of 1 μm. Finally, the precipitate was dried in a muffle furnace at a temperature of 75°C for 24 hours. The precipitate obtained in such a manner was denoted as simulated copper plating sludge. Before the sulfidation experiments, the simulated copper plating sludge was thoroughly ground and screened using sieves with mesh diameters of 32 μm, 45 μm, 63 μm, 75 μm and 125 μm.

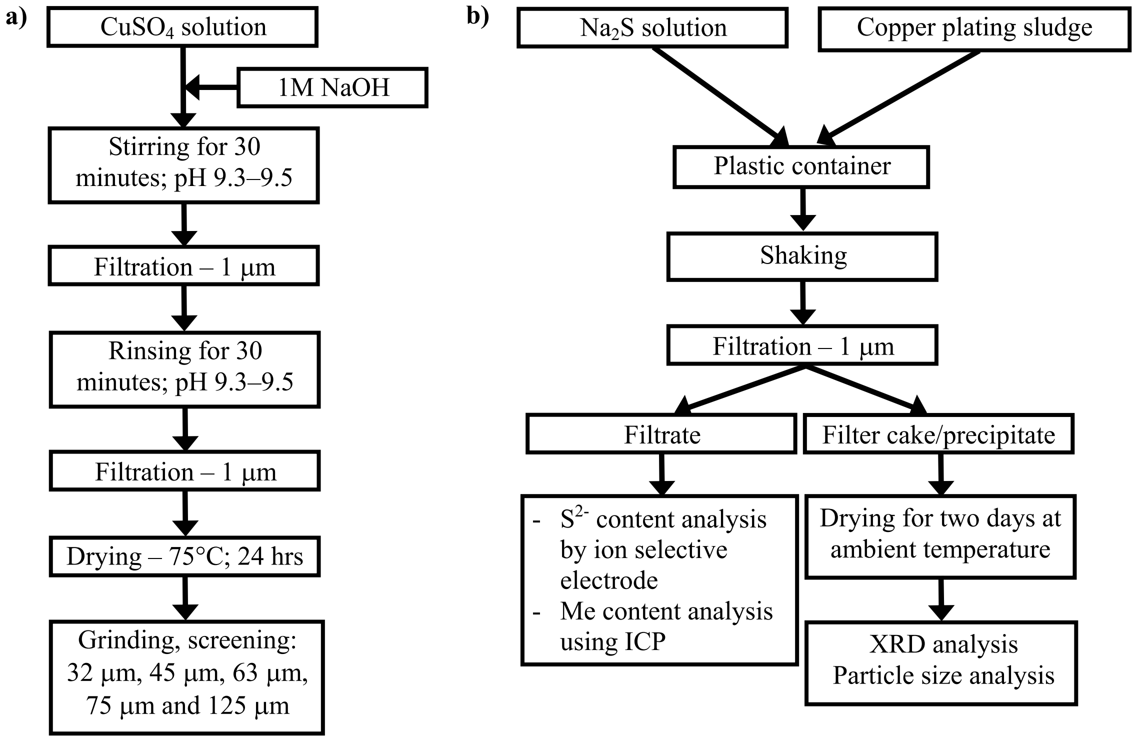


Fig. 3.1: Experimental flow chart of preparation of simulated copper plating sludge – Fig. 3.1(a) and sulfidation treatment – Fig. 3.1(b)

3.2.1.2 Real copper plating sludge

The sample of real copper plating sludge acquired from Sanshin MFG. Co., Ltd., Japan was used. In a similar way to that of simulated copper plating sludge, the real plating sludge was dried in a muffle furnace at a temperature of 75°C for 24 hours, and then thoroughly ground and screened using sieves with mesh diameters of 32 μm, 45 μm, 63 μm, 75 μm and 125 μm.

3.2.2 Determination of plating sludge composition

The elemental composition of the simulated and real copper plating sludge was determined in triplicate by dissolving 100 mg of each sample in aqua regia (a mixture of HCl and HNO_3 at a ratio of 3:1). Then, the solutions arising thereof were analyzed using inductively coupled plasma (ICP, Vista-MPX Simultaneous ICP-OES, Varian, Inc.). The composition of both plating sludges is given in **Table 3.1**. It can be seen that the copper content in simulated plating sludge was more than twice higher than that of real plating sludge. In addition, other heavy metals such as nickel, zinc, lead etc., as well as high amounts of sodium and calcium were found in real copper plating sludge.

Table 3.1: Composition of real and simulated copper plating sludge

	Simulated sludge Content [mg/g]	Real sludge Content [mg/g]
Cu	623±11.9	257±8.75
Cd	-	1.02±0.01
Cr	-	2.30±0.01
Fe	-	3.60±0.16
Mn	-	0.39±0.01
Ni	-	48.2±1.12
Pb	-	12.7±0.15
Sn	-	15.6±0.59
Zn	-	19.5±0.51
Na	8.20±0.29	28.6±0.94
Ca	-	46.8±1.42
K	-	0.57±0.04

Furthermore, in order to analyze the crystallographic composition, the samples were subjected to X-ray powder diffraction (XRD) analysis with scanning mode of $2\theta/\theta$, under the condition of 50 kV/100 mA (RINT-2500 TTR, Rigaku Model). Finally, in the case of simulated copper plating sludge, the amount of copper sulfate remaining in the sludge in copper hydroxide sulfates was determined by means of thermogravimetric analysis (TGA-50, Shimadzu Corporation, Japan) under N_2-O_2 atmosphere (ratio of N_2:O_2 of 4:1), at a gas flow rate of 50 mL/min and a heating rate of 2°C/min.

3.2.3 Treatment procedure

The sulfidation treatment of both sludges was carried out in a batch system, according to the diagram shown in **Fig. 3.1(b)**. A volume of 50 mL aqueous Na_2S solution, prepared by dissolving $Na_2S \cdot 9H_2O$ of reagent grade (Wako Pure Chemical Industries, Ltd.) in distilled water to adjust the initial molar ratio of S^{2-} to Me^{2+} to 1.00, 1.25 or 1.50, was poured into a plastic container. In the case of copper simulated sludge, Me^{2+} stands only for Cu^{2+}, and thus the molar ratio of S^{2-} to Me^{2+} is referred to as S^{2-} to Cu^{2+} molar ratio. By contrast, in the case of real plating sludge, the initial molar ratio of S^{2-} to Me^{2+} of 1.50, 1.25 or 1.00 refers to the sum of all heavy metals present in the real sludge (**Table 3.1**). In the next step, an appropriate amount of the sludge was charged into each plastic container adjusting a solid to liquid (S:L) ratio to 1.00:50 (sample weight concentration of about 20 g/L). Then, the plastic containers were shaken on a vertical shaker for a period of 5 minutes to 24 hours. Finally, the slurry was filtered with a 1 μm pore size filter paper.

3.2.4 Analyses of filtrates and filter cakes

The filtrates were subjected to the determination of heavy metals using ICP. The concentration of sulfide ions remaining in the filtrates was measured by S^{2-} ions selective electrode (S-125, Ion meter IM-55G, DKK-TOA Corp.). In the measurements of residual concentrations of S^{2-} ions, the pH of the sample solution was kept at a value higher than 13.0, in accordance with the standard procedure for the measurement of S^{2-} ions, and then, the ionic strength of the sample solution was adjusted by L-ascorbic acid.

The filter cakes were dried at an ambient temperature of about 25°C for 2 days, and then subjected to X-Ray powder diffraction (XRD) analysis. In addition, the particle size distribution of sulfidation products was measured by means of a laser scattering particle size distribution analyzer (Horiba LA-920, Horiba Ltd., Tokyo, Japan).

3.2.5 Determination of oxidation-reduction potential

The oxidation-reduction potential (ORP) of the reacting system was measured using an ORP electrode (PST-5721C, DKK-TOA Corp.). The ORP electrode was immersed into the plastic container filled with Na_2S solution, which was placed on a magnetic stirrer, to obtain the initial ORP value. Subsequently, a 1 gram of the copper sludge was charged into the plastic container adjusting a solid to liquid (S:L) ratio to 1.00:50, and the change in the ORP value during sulfidation was recorded continuously. To avoid the consumption of sulfide ions in the sample solution by oxidation, the plastic container, with the ORP electrode immersed inside, was sealed with a wrap film.

3.3 Results and discussion

3.3.1 Sulfidation behaviour of simulated copper plating sludge

3.3.1.1 Effect of S^{2-} to Cu^{2+} ratio on the composition of sulfidation products

The simulated plating sludge screened to a particle size lower than 32 μm was contacted with Na_2S solution at the initial molar ratios of S^{2-} to Cu^{2+} of 1.00, 1.25 and 1.50, which corresponded to the pH value of the reacting system of 13.15, 13.25 and 13.30, respectively. In this work, no pH adjustment was performed and the pH value of the reacting system resulted from the amount of $Na_2S{\cdot}9H_2O$ dissolved in distilled water to adjust an initial molar ratio of S^{2-} to Cu^{2+}. **Figure 3.2** shows the time change of the consumption of S^{2-} ions at different S^{2-} to Cu^{2+} molar ratios obtained for simulated copper plating sludge.

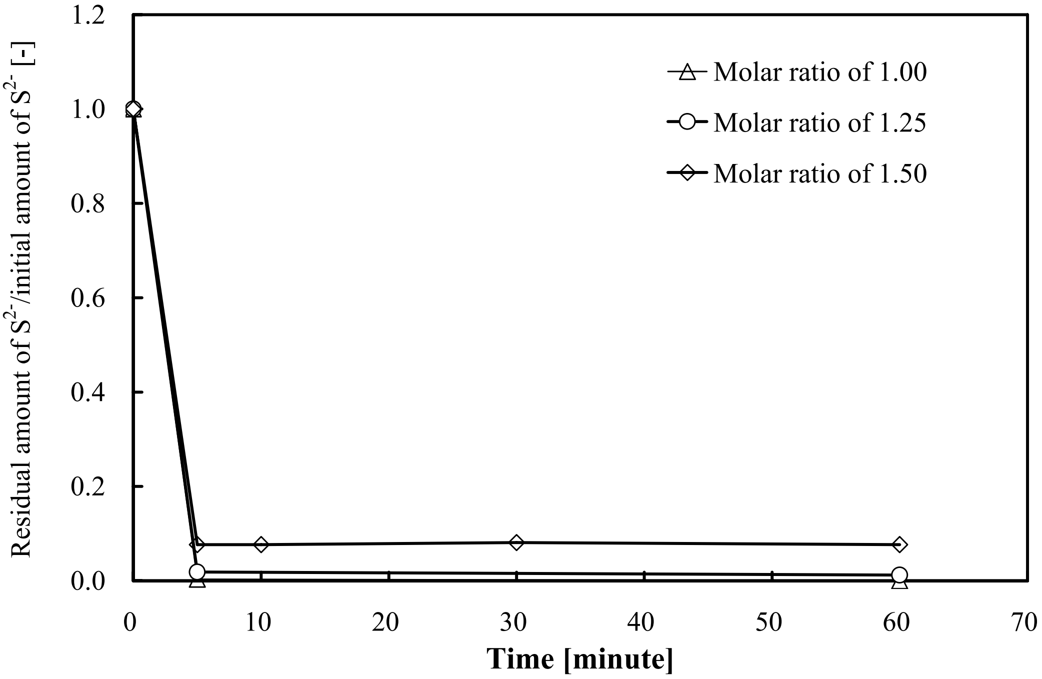


Fig. 3.2: Time change of residual concentration of S^{2-} ions for simulated copper plating sludge

It can be seen from the figure that S^{2-} ions were almost completely consumed within the first 5 minutes, which indicated a high reaction rate of sulfidation of copper compounds to copper sulfides. Similar to this study, the high sulfidation rate has been reported for the sulfidation of brochantite [$Cu_4(OH)_6SO_4$] and chrysocolla [$CuO\cdot SiO_2\cdot 2H_2O$] with ammonium sulfide [4], further for the sulfidation of chrysocolla and malachite [$CuCO_3\cdot Cu(OH)_2$] with sodium sulfide [5], and for the sulfidation treatment of malachite with sodium sulfide and sodium tetrasulfide [6]. However, in the reported research works, the sulfidation rate of oxidized copper ores was found to be the highest at mildly acidic or neutral pH, and the sulfidation rate significantly decreased when the pH value was increased to a value of about 11.0. In particular, Raghavan *et al.* [4] reported that at the pH value of 7.4, the sulfide ions were consumed within the first 5 minutes of contacting brochantite with ammonium sulfide, while at a pH value of 10.5, a contacting time of 30 minutes was required. By contrast, a high sulfidation rate was obtained in this study at the pH value higher than 13.0 for the simulated copper plating sludge containing a mixture of brochantite, posnjakite and copper hydroxide. It is considered that the difference in the sulfidation rate resulted from a significantly lower crystallinity of minerals involved in plating sludge compared to that of copper ores. Hence, the crystals of brochantite, posnjakite and copper hydroxide involved in simulated copper plating sludge were more susceptible to sulfidation treatment and therefore a high reaction rate was achieved resulting in the complete sulfidation within the first 5 minutes.

To identify the products of sulfidation reactions, the XRD analysis of sulfidation products was carried out and the results are shown in **Fig. 3.3**, together with XRD patterns of raw simulated copper plating sludge.

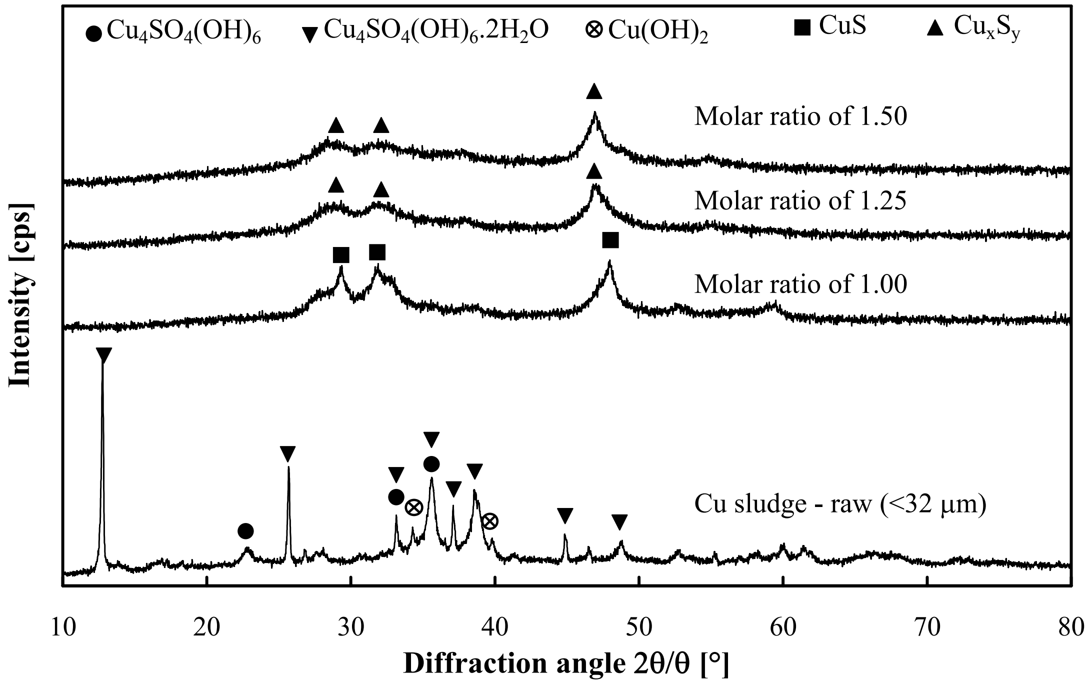


Fig. 3.3: XRD patterns of simulated copper plating sludge obtained after 5 minutes at different S^{2-} to Cu^{2+} molar ratios

At first, as shown in this figure, the presence of $Cu(OH)_2$, posnjakite [$Cu_4SO_4(OH)_6 \cdot 2H_2O$], and brochantite [$Cu_4SO_4(OH)_6$] was confirmed in the raw simulated copper plating sludge. The amount of copper sulfate remaining in the sludge in copper hydroxide sulfates was determined by means of TG analysis. It was found that the crystalline water was evaporated in the temperature range of 140ºC to 380ºC and then the remaining $CuSO_4$ of posnjakite and brochantite was decomposed to CuO in the temperature range of 580ºC to 710ºC. Based on the weight loss accompanying the decomposition of $CuSO_4$ to CuO, the amount of $CuSO_4$ remaining in copper hydroxide sulfates was estimated to be about 13.5 wt%.

Then, when the simulated copper plating sludge contacted with Na_2S at the S^{2-} to Cu^{2+} molar ratio of 1.00 was analyzed using XRD, the cupric (Cu^{2+}) sulfide was found as the main product of sulfidation, while no peaks of the raw sludge were observed. From this result, it was considered that cupric ions of copper hydroxide, brochantite and posjankite reacted with S^{2-} ions to yield CuS at a molar ratio of S^{2-} to Cu^{2+} of 1.00, as expressed by Eq. (3.1).

$$Cu^{2+} + S^{2-} \rightleftharpoons CuS(s) \qquad \Delta G(298K) = -204.8 \text{ kJ/mol} \qquad (3.1)$$

By contrast, various cuprous (Cu^{+}) sulfides, such as Cu_2S, Cu_7S_4, Cu_8S_5 and $Cu_{31}S_{16}$ with a molar ratio of copper to sulfur of about 2 to 1 were formed when the sulfidation experiments were conducted at S^{2-} to Cu^{2+} molar ratio of 1.25 and 1.50. This result suggests that the cupric ions were, at first, reduced to cuprous ions and were subsequently precipitated as various cuprous (Cu^{+}) sulfides. Based on this result, it was considered that, at higher S^{2-} to Cu^{2+} molar ratios, the sulfidation of copper occurred according to the following reactions expressed by Eqs. (3.2) and (3.3).

$$2Cu^{2+} + 2S^{2-} \rightleftharpoons 2Cu^{+} + S_2^{2-} \qquad \Delta G(298K) = -123.1 \text{ kJ/mol} \qquad (3.2)$$

$$2Cu^{+} + S^{2-} \rightleftharpoons Cu_2S \qquad \Delta G(298K) = -272.4 \text{ kJ/mol} \qquad (3.3)$$

$$2Cu^{2+} + 3S^{2-} \rightleftharpoons Cu_2S(s) + S_2^{2-} \qquad \Delta G(298K) = -395.5 \text{ kJ/mol} \qquad (3.4)$$

The Eq. (3.2) shows the oxidation-reduction reaction of Cu^{2+} (reduced to Cu^{+}) with S^{2-} (oxidized to S_2^{2-}) followed by the precipitation of Cu_2S as expressed by Eq. (3.3). The Eq. (3.4) summarizes the overall reaction mechanism and Gibbs free energy of this reaction (calculated using HSC Chemistry Ver.3.02) was found to be -395.5 kJ/mol, which was almost twice greater than the Gibbs free energy of the reaction given by Eq. (3.1). Thus, from thermodynamic point of view, it was considered that the sulfidation of copper should proceed via Eqs. (3.2) and (3.3) rather than Eq.(3.1).

3.3.1.2 Effect of ORP on sulfidation of copper

In order to clarify the mechanism of sulfidation of copper, the ORP measurements were carried out and the results expressed in terms of ORP against standard hydrogen electrode are shown in **Fig. 3.4**.

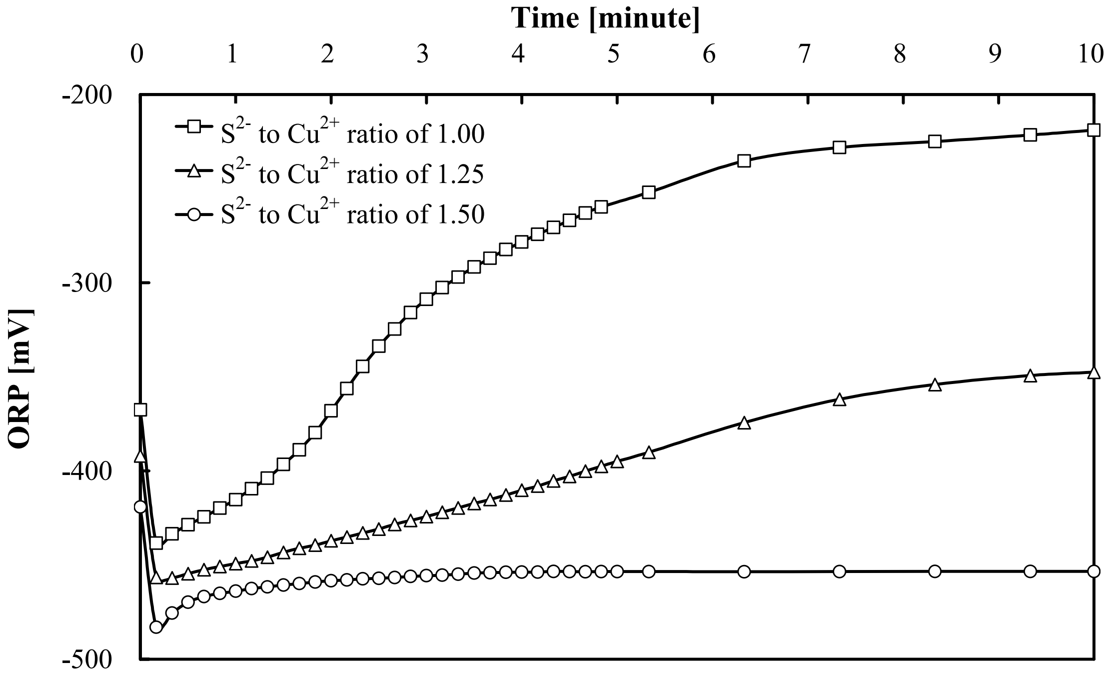


Fig. 3.4: Time change of oxidation-reduction potential for simulated copper plating sludge

In this figure, it can be seen that the ORP value steeply decreased when the sludge was added to the plastic container filled with Na_2S solution, irrespective of S^{2-} to Cu^{2+} molar ratio. The decrease in the ORP value was caused by the oxidation half reaction (Eq. (3.5)), which coexisted with the reduction half reaction of Cu^{2+} to Cu^{+} given by Eq. (3.6).

$$2S^{2-} \rightleftharpoons S_2^{2-} + 2e^- \qquad E_{o[S_2^{2-}/S^{2-}]} = -0.478\,V \qquad (3.5)$$

$$2Cu^{2+} + 2e^- \rightleftharpoons 2Cu^+ \qquad E_{o[Cu^{2+}/Cu^+]} = 0.160\,V \qquad (3.6)$$

By using the Nernst equation for half reaction given by Eq. (3.5), the ORP can be determined using Eq. (3.7).

$$E = E_o - \frac{RT}{nF}\ln\frac{a_{S^{2-}}^2}{a_{S_2^{2-}}} \qquad (3.7),$$

where E [V] is the oxidation reduction potential (ORP) of the reacting system, E_o is the standard oxidation reduction potential of S_2^{2-}/S^{2-} couple [V], R is gas constant [J/(K mol)], T is absolute temperature [K], n is the number of electrons transferred [-], F is the Faraday's constant [C/mol], $a_{S^{2-}}$ is the activity of S^{2-} ions [-] and $a_{S_2^{2-}}$ is the activity of S_2^{2-} ions [-]. Inserting the value of E_o for S_2^{2-}/S^{2-} couple and n to Eq. (3.7), and further assuming that the activity coefficients of S_2^{2-} and S^{2-} are equal to one, gives Eq. (3.8)

$$E = -0.478 - \frac{RT}{2F}\ln\frac{\left[S^{2-}\right]^2}{\left[S_2^{2-}\right]} \qquad (3.8),$$

where $[S^{2-}]$ is the concentration of S^{2-} ions and $[S_2^{2-}]$ is the concentration of S_2^{2-} ions.

At the beginning of the sulfidation, the conversion is negligible, and thus, the concentration of S_2^{2-} ions is assumed to be almost zero. Hence, the initial ORP value calculated by Eq. (3.8) becomes almost negative infinite, which explained the steep decrease in ORP value shown in **Fig. 3.4**. Subsequently, the concentration of S_2^{2-} increased with the progress of sulfidation reactions resulting in an increase in oxidation-reduction potential, as also shown in **Fig. 3.4**.

Further, the stability as well as the formation of copper sulfides of Cu_2S and CuS strongly depends on the pH and potential values of the reacting system. Therefore, an Eh-pH diagram (Eh stands for oxidation-reaction potential) of Cu-S-H_2O system was constructed based on the assumption that only copper compounds of Cu, CuS, Cu_2S and

$Cu_4SO_4(OH)_6$ were present in reacting system [4]. **Figure 3.5** shows the Eh-pH diagram constructed for S^{2-} to Cu^{2+} molar ratio of 1.50 and a temperature of 298.15K by using the thermodynamic data given in **Table 3.2**.

Table 3.2: Thermodynamic data for Eh-pH diagram

Species (state)	ΔG_f^o [kJ/mol]	Reference
H_2O (liq)	-237.19	[7]
H_2S (aq)	-27.82	[7]
HS^- (aq)	12.09	[7]
S^{2-} (aq)	85.81	[7]
Cu (c)	0.00	[7]
Cu_2S (c)	-53.60	[7]
CuS (c)	-86.19	[7]
$Cu_4SO_4(OH)_6$	-1818.45	[8]

In this diagram, the potential boundary between Cu_2S and CuS at the pH range of 12.9 to 14.0 was determined based on the Eq. (3.9)

$$2CuS(s) + 2e^- \leftrightharpoons Cu_2S(s) + S^{2-} \quad (3.9).$$

In the given pH range, sulfide ions are present in the solution in the S^{2-} form, and therefore, the Cu_2S/CuS potential boundary is not affected by the pH value of the reacting system. The value of oxidation-reduction potential for Cu_2S/CuS potential boundary is then determined using the Nernst equation expressed by Eq. (3.10)

$$E = -0.554 - \frac{RT}{2F}\ln\left[S^{2-}\right] \quad (3.10)$$

where the value of -0.554 V represents the value of standard oxidation reduction potential of Cu_2S/CuS couple [V], calculated using the thermodynamic data given in **Table 3.2**.

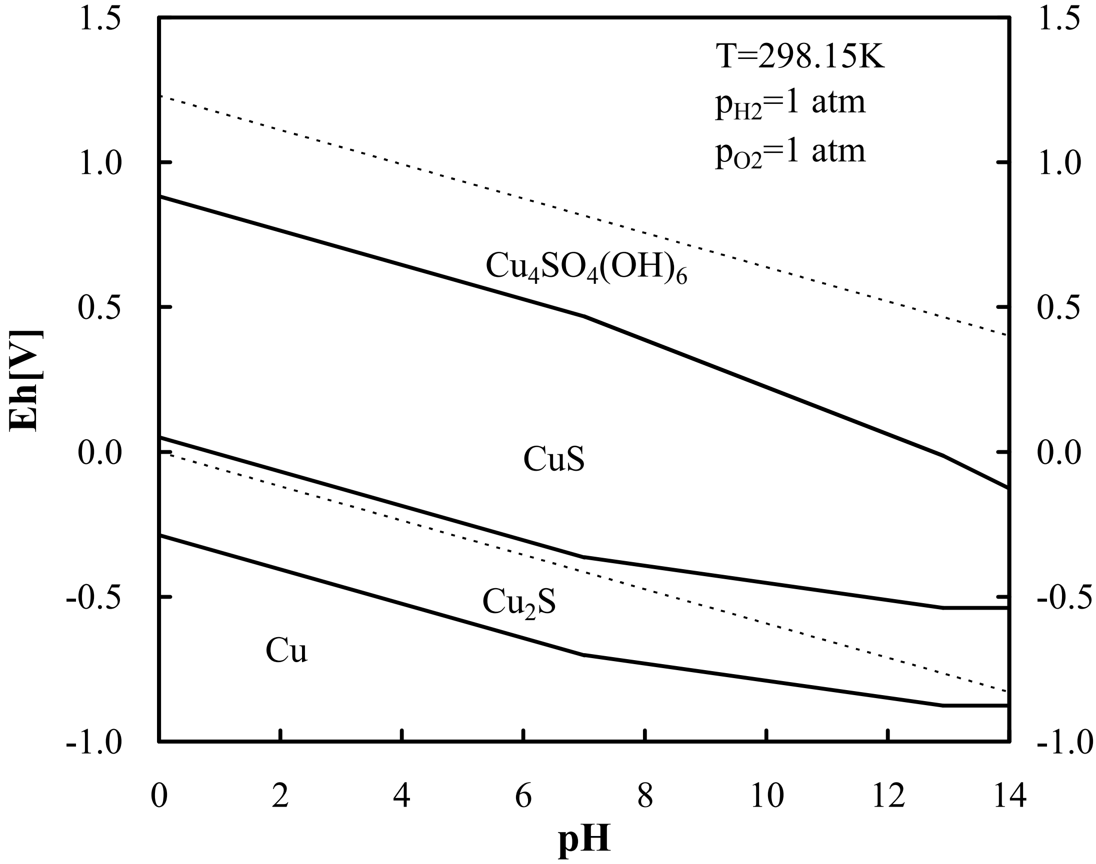


Fig. 3.5: Eh-pH diagram of Cu-S-H_2O system at 298.15K

It can be seen that at a constant temperature, the value of Cu_2S/CuS potential boundary depends only on the concentration of S^{2-} ions. Subsequently, the potential boundary between Cu_2S and CuS was calculated to be -0.538 V at the S^{2-} to Cu^{2+} molar ratio of 1.50 (pH value of 13.30), and the value just slightly increased to -0.536 V at the molar ratio of S^{2-} to Cu^{2+} of 1.25 (pH value of 13.25). Based on the ORP results obtained for the molar ratios of S^{2-} to Cu^{2+} of 1.25 and 1.50 (**Fig. 3.4**), it was considered that the potential, at first, dropped below the Cu_2S/CuS boundary leading to the formation of Cu_2S rather than CuS. Then, as a consequence of a higher conversion, the ORP of the reacting system increased to a value of about -0.460 V at the molar ratio of S^{2-} to Cu^{2+} of 1.50, which brought about a shift in the ORP value from the stability region of Cu_2S to the stability region of CuS. As a result of the shift in the ORP value of the reacting system, a gradual conversion of Cu_2S to CuS was supposed to occur. Therefore, to support this conclusion, the contacting period of the simulated copper plating sludge with Na_2S was further extended up to 24 hours at the molar ratio of S^{2-} to Cu^{2+} of 1.50.

Figure 3.6 shows the XRD patterns of sulfidation products obtained and it is shown that Cu_xS_y was indeed partially converted to CuS after 24 hours, which supported the above given conclusion.

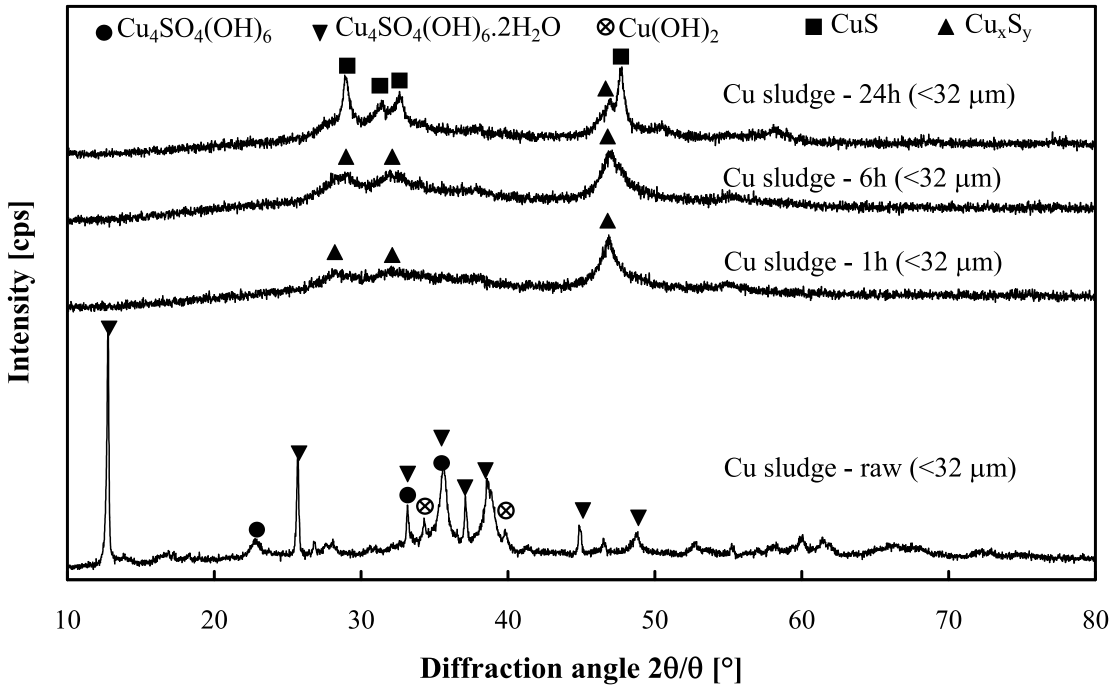


Fig. 3.6: XRD patterns of simulated copper plating sludge obtained at S^{2-} to Cu^{2+} ratio of 1.50, after different time

In the case of S^{2-} to Cu^{2+} molar ratio of 1.00 (**Fig. 3.4**), the initial decrease in the ORP value was lower compared to those of S^{2-} to Cu^{2+} molar ratios of 1.25 and 1.50. Hence, it is assumed that the ORP value at the beginning of the sulfidation did not drop below the potential boundary of Cu_2S/CuS, which was calculated to be -0.533 V for this S^{2-} to Cu^{2+} molar ratio. Consequently, the copper compounds in the plating sludge were rather converted to CuS than to Cu_2S.

3.3.2 Sulfidation behaviour of real copper plating sludge

3.3.2.1 Effect of S^{2-} to Me^{2+} ratio on the composition of sulfidation products

The sulfidation treatment of real plating sludge was conducted in the same way as that of simulated sludge. The molar ratio of S^{2-} to Me^{2+} was adjusted to 1.00, 1.25 or 1.50, where Me^{2+} stands for the sum of all heavy metals involved in the sludge (**Table 3.1**). The pH values of the reacting systems were 12.91, 13.01 and 13.10 for S^{2-} to Me^{2+} molar ratios of 1.00, 1.25 and 1.50, respectively. **Figure 3.7** shows the time change of the residual concentration of S^{2-} ions for different molar ratios of S^{2-} to Me^{2+}.

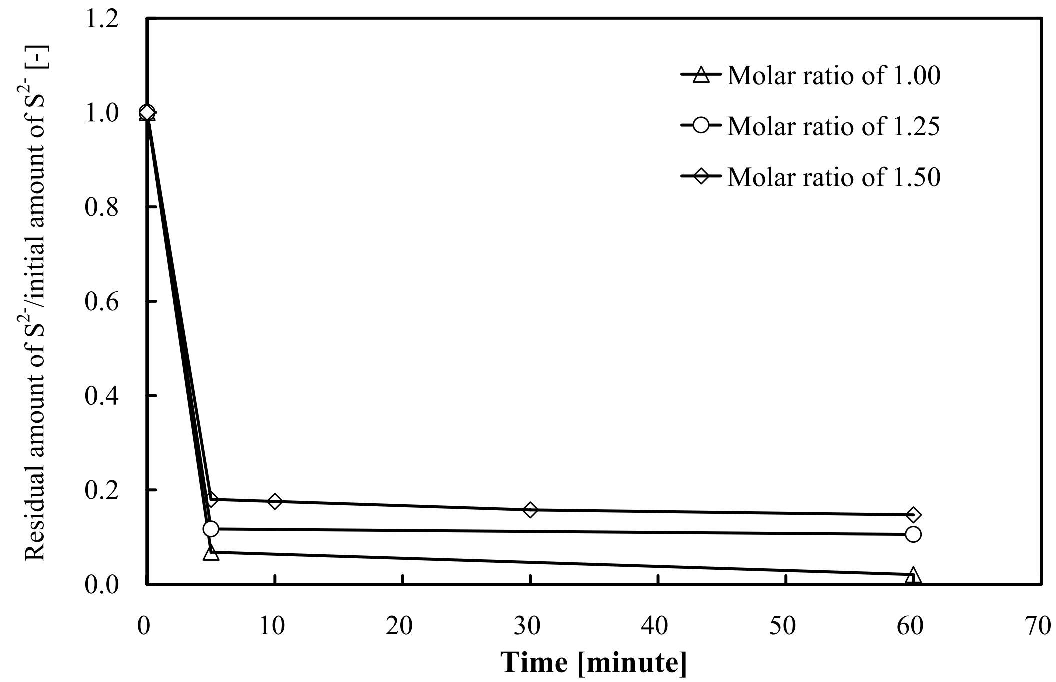


Fig. 3.7: Time change of residual concentration of S^{2-} ions for real copper plating sludge

As shown in this figure, S^{2-} ions were almost completely consumed within a short period of 5 minutes indicating a high sulfidation rate of copper compounds, which was similar to the results obtained for simulated plating sludge (**Fig. 3.2**), except that the residual concentrations of S^{2-} ions were kept higher. This difference in the residual concentration of S^{2-} ions between the simulated plating sludge and the real plating sludge was attributed to lower sulfidation rates of heavy metals such as nickel and zinc contained in the real plating sludge, as reported in Chapter 2. Further, the concentrations of the heavy metals in the filtrates were determined by ICP and it was found that the concentrations of copper and nickel were kept below 2 mg/L, while the concentrations of zinc, iron, lead, etc. were kept below 0.1 mg/L (the lowest standard used in ICP analyses).

To identify the crystallographic composition of sulfidation products, the XRD analysis of the sulfidation products of the real plating sludge, was carried out. **Figure 3.8** shows the XRD patterns obtained and it was found that CuS was formed as the main sulfidation product within 5 minutes, irrespective of S^{2-} to Me^{2+} molar ratio. While, no characteristic XRD peaks of copper compounds were observed for the raw sample of real plating sludge indicating a low crystallinity of the copper compounds.

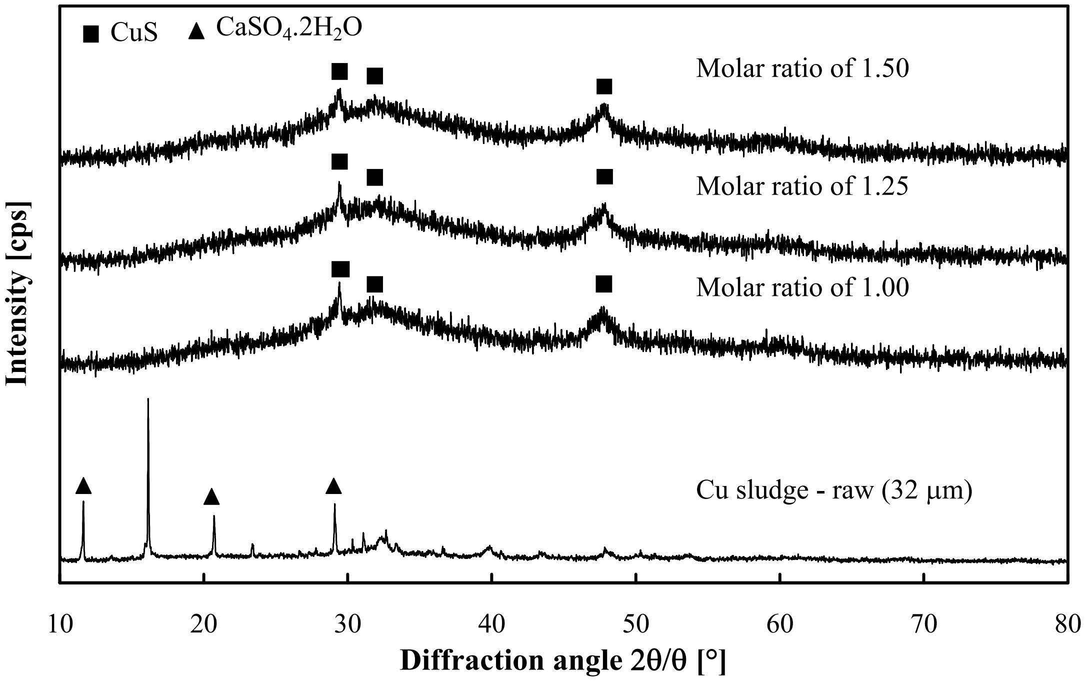


Fig. 3.8: XRD patterns of real copper plating sludge obtained after 5 minutes at different S^{2-} to Me^{2+} molar ratios

3.3.2.2 Effect of ORP on sulfidation of copper

Figure 3.9 shows the time change of ORP of the reacting system of real plating sludge during sulfidation treatment. In the case of simulated plating sludge (**Fig. 3.4**), the potential steeply dropped to a value of about -0.490 V and then increased to a value of about -0.460 V, at S^{2-} to Cu^{2+} molar ratio of 1.50. To the contrary, somewhat different behaviour was obtained for real plating sludge at S^{2-} to Me^{2+} molar ratio of 1.50, as shown in **Fig. 3.9**. It can be seen that the potential decreased more slowly, compared to that of simulated plating sludge, basically to attain a value of about -0.455 V at the S^{2-} to Me^{2+} molar ratio of 1.50. It was considered that the difference in ORP behaviour observed between the simulated plating sludge and the real plating sludge resulted from the presence of other ions in the reacting system. Given the difference in the ORP behaviour, it was assumed that the potential value of the reacting system was kept above the Cu_2S/CuS potential boundary, which led to the formation CuS rather than Cu_2S. The Cu_2S/CuS potential boundary was determined to be -0.531 V, in the case of S^{2-} to Me^{2+} molar ratio of 1.50 and the corresponding pH value of 13.10.

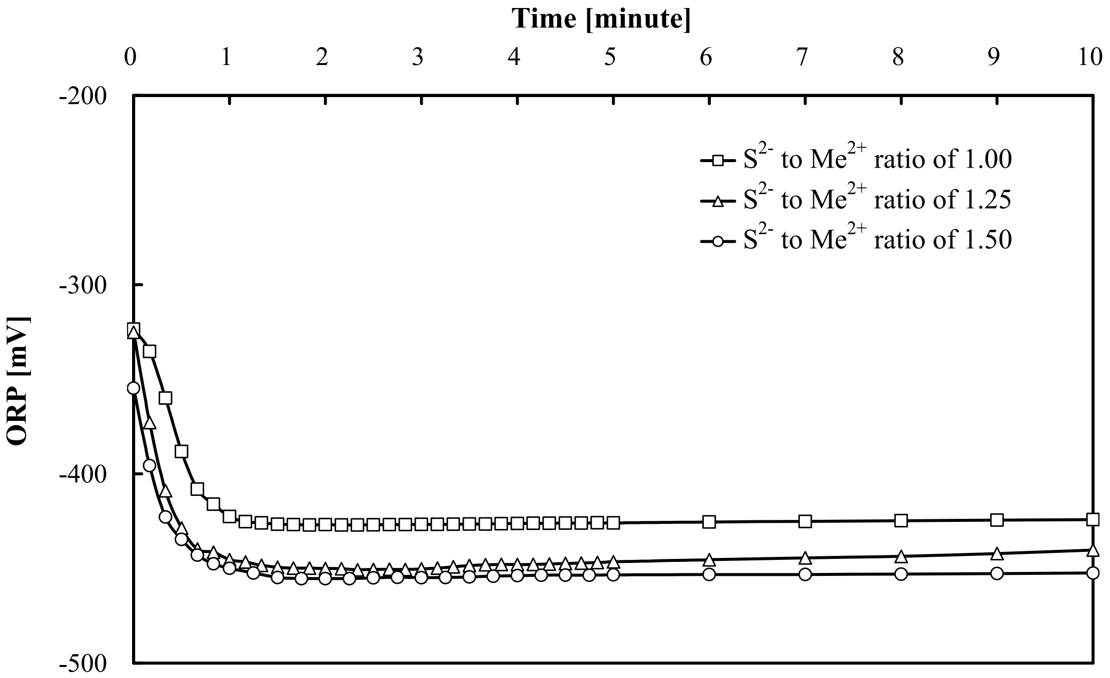


Fig. 3.9: Time change of oxidation-reduction potential for real copper plating sludge

3.3.3 Effect of particle size on sulfidation of copper sludges

In order to study the effect of particle size on the sulfidation of copper compounds to copper sulfides, the experiments were conducted for the simulated and real plating sludge screened to the particle size ranges of 0-32 μm, 45-63 μm and 75-125 μm. The molar ratio of S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} for the real plating sludge) was fixed at 1.50 and the sulfidation time was set at 1 hour. **Figure 3.10** presents the XRD patterns of the sulfidation products obtained for the simulated plating sludge and the real plating sludge. As can be seen in the figure, no significant difference in the XRD patterns of simulated and real plating sludge was observed when the particle size was increased from a smaller particle size of 0 to 32 μm to a larger particle size of 75 to 125 μm. Thus, it was concluded that the conversion of copper compounds to copper sulfides, in the particle size range used, was not dependant on the particle size. Lower intensities of XRD peaks of copper sulfides in the case of the real plating sludge compared to those of simulated plating sludge were attributed to a lower crystallinity of the copper sulfides formed.

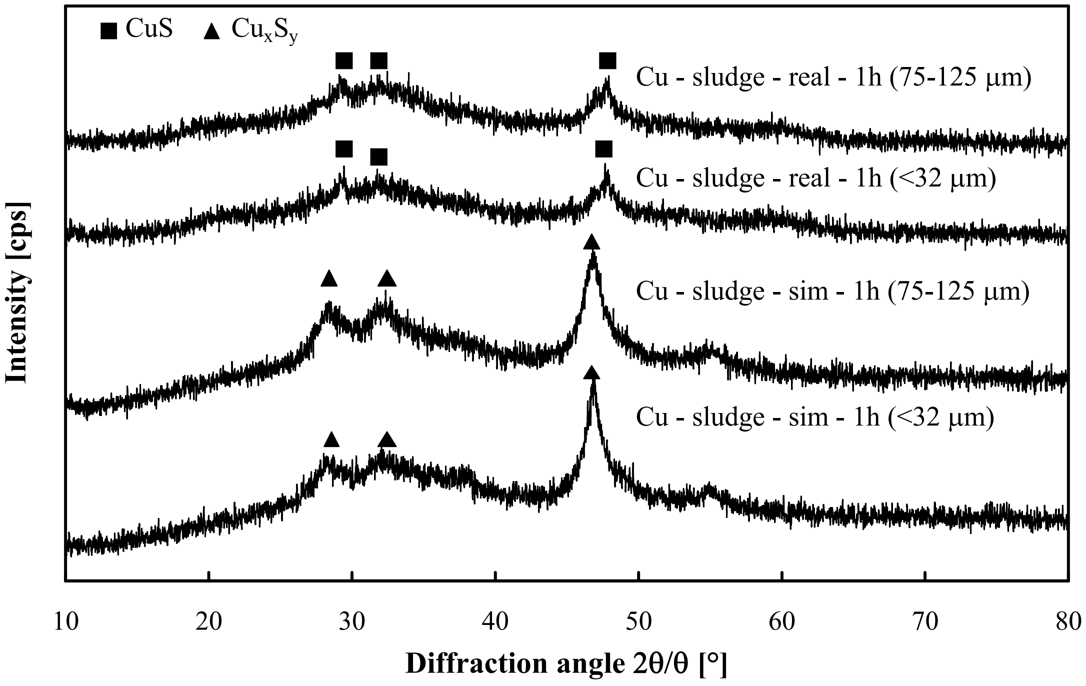


Fig. 3.10: XRD patterns of simulated- and real- copper plating sludge obtained for different particle size of initial sludge

3.3.4 Particle size analysis of sulfidation products of copper sludges

Figure 3.11 shows the particle size distribution of the sulfidation products formed at the molar ratio of S^{2-} to Cu^{2+} of 1.50 (S^{2-} to Me^{2+} for the real plating sludge) and the sulfidation time of 1 hour.

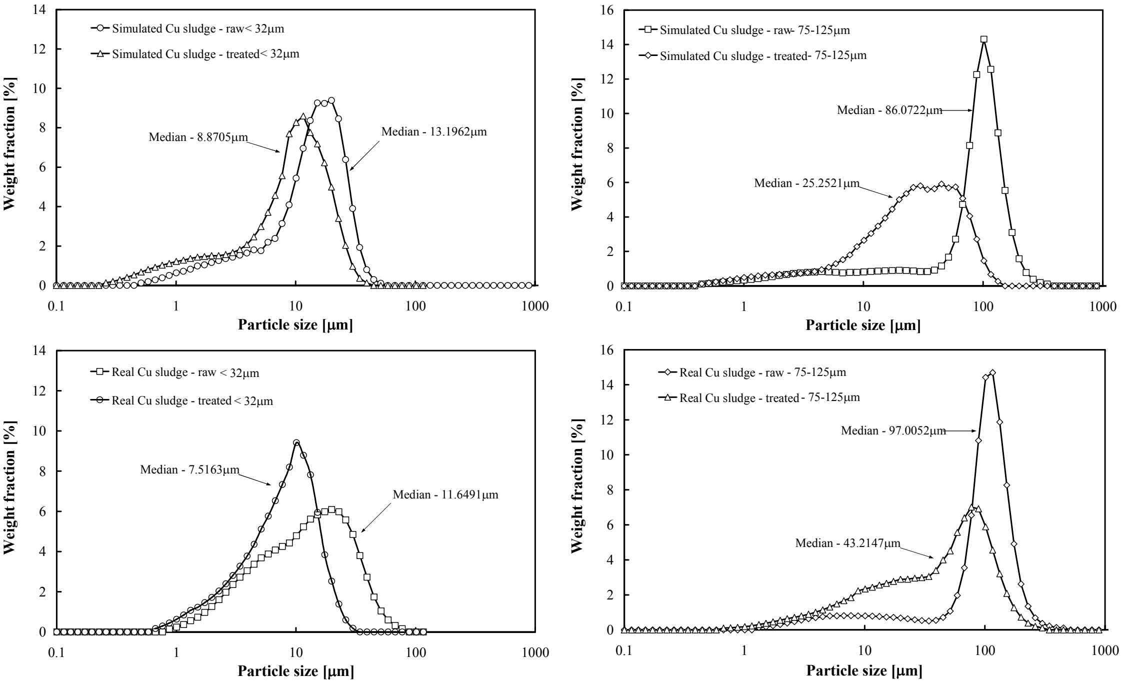


Fig. 3.11: Particle size distribution analyses of sulfidation products of simulated- and real- copper plating sludge

As can be seen in the figure, the particle size of sulfidation products was remarkably affected by the initial particle size of the raw sludge. In the case of particle size of raw sludges of 0 to 32 μm, the average particle sizes of the sulfidation products were 8.87 μm and 7.52 μm for simulated and real copper plating sludge, respectively. By contrast, the average particle sizes of sulfidation products of 25.25 μm for simulated copper plating sludge and 43.21 μm for real copper plating sludge were obtained when the particle size of the raw sludge in the range of 75 to 125 μm was chosen. From these findings, it is concluded that the conversion of Cu compounds to copper sulfides rather started with the formation of copper sulfides on the surface of the original sludge particles than with the precipitation of new particles of copper sulfides in the solution.

This result is in agreement with the findings reported for malachite, where the copper sulfides were found to quickly form a primary layer on the malachite specimen and subsequently a secondary layer enclosing unreacted malachite inside [6]. Similarly, Castro *et al.* [7] reported that in the sulfidation treatment of CuO, the sulfide ions were at first adsorbed on the surface of CuO particles followed by the reaction of sulfide ions with CuO. However, in this study, an amount of unreacted sample enclosed under the sulfide layer is assumed to be negligible, since no XRD peaks of raw sample were found when the simulated copper sludge contacted with Na_2S was subjected to XRD analysis.

Finally, the reduction in the particle size during sulfidation treatment was attributed to the disintegration of the original sludge present in the form of agglomerates of particles as fine as 1 μm.

3.4 Conclusions

The sulfidation treatment of simulated and real copper plating sludge was carried out at S^{2-} to Cu^{2+} (S^{2-} to Me^{2+}) molar ratios of 1.00, 1.25 and 1.50, for a period of 5 minutes to 24 hours. Some concluding findings obtained in this study are summarized as follows:

- The copper compounds involved in simulated and real plating sludge were easily converted to copper sulfides within the first 5 minutes of contacting the sludges with Na_2S.

- The XRD analyses of sulfidation products of simulated copper plating sludge obtained after sulfidation treatment for 5 minutes showed that the formation of copper sulfides is strongly affected by S^{2-} to Cu^{2+} molar ratio used. In the case of S^{2-} to Cu^{2+} molar ratio of 1.00, cupric sulfide of CuS was identified as the main sulfidation product, while various cuprous sulfides such as Cu_2S, Cu_7S_4, Cu_8S_5, $Cu_{31}S_{16}$ were formed at S^{2-} to Cu^{2+} molar ratio of 1.25 and 1.50. The formation of various copper sulfides was attributed to the changes in ORP of the reacting system at different S^{2-} to Cu^{2+} molar ratios.

- In the sulfidation treatment of real plating sludge, cupric sulfide of CuS was found as the main sulfidation product irrespective of S^{2-} to Me^{2+} molar ratio, which was attributed to a different ORP behaviour compared to that of simulated copper plating sludge.

- The effect of particle size of the initial sludge was investigated in the range of 0 to 125 μm, at the S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} for the real plating sludge) molar ratio of 1.50. It was found that the conversion was independent of the particle size of the initial sludge used.

- The particle size distribution analysis of sulfidation products contacted with Na_2S for 1 hour at the molar ratio of S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} for the real plating sludge) of 1.50 showed that particle size distribution of sulfidation products strongly depended on the initial particle size of the raw sludges.

3.5 Nomenclature

$[S^{2-}]$	concentration of S^{2-} ions [mol/L]
$[S_2^{2-}]$	concentration of S_2^{2-} ions [mol/L]
$a_{S^{2-}}$	activity of S^{2-} ions [-]
$a_{S_2^{2-}}$	activity of S_2^{2-} ions [-]
ΔG	Gibbs free energy [kJ/mol]
ΔG_f^0	Gibbs free energy of formation [kJ/mol]
E	oxidation-reduction potential of the reacting system [V]
E_o	standard oxidation-reduction potential of S_2^{2-}/S^{2-} couple [V]
F	Faraday's constant [C/mol],
n	number of electrons transferred [-]
R	gas constant [J/(K mol)]
T	temperature [K]

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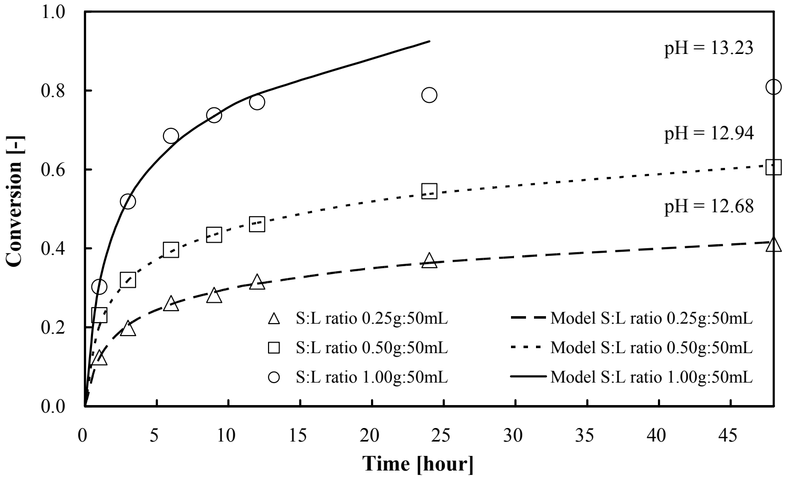
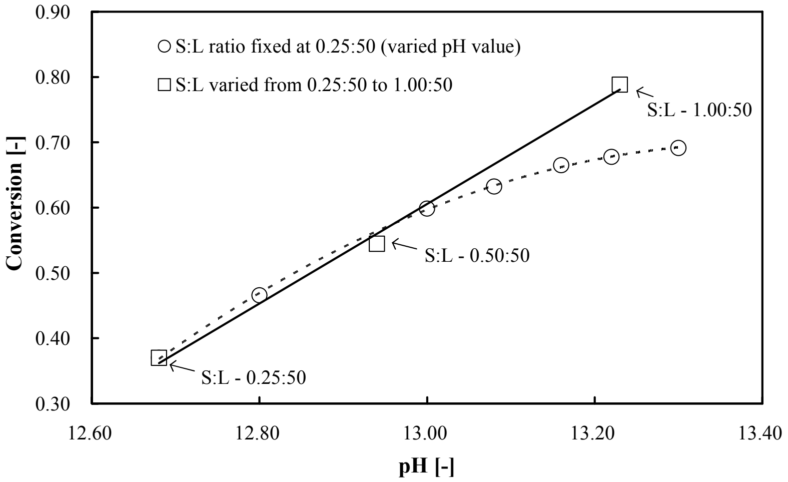
CHAPTER 4

Sulfidation treatment of zinc plating sludges





In this chapter, the sulfidation treatment was conducted for simulated zinc plating sludge and real plating sludge containing high amount of zinc in order to confirm the results obtained for ZnO. Similarly to ZnO, the conversion was found to be strongly dependant on S:L ratio (pH value of the reacting system) and a maximum conversion of 80.9% was obtained after 48 hours at an S:L ratio of 1.00:50 (pH of 13.23). The XRD analysis of sulfidation product obtained under such conditions showed only peaks of ZnS suggesting that the rest of zinc sludge remained unreacted inside the agglomerates of ZnS. Finally, the results obtained with real plating sludge confirmed that zinc compounds can be converted to ZnS.

4.1 Introduction

Electroplating is a technique used in surface finishing of metals, ceramics and plastics. In Japan, heavy metals such as zinc, copper, nickel, chromium and tin are commonly used and zinc accounts for more than 30% (6,054 tons/year) of the total amount of metals consumed [1]. In Chapter 2, the sulfidation treatment with Na_2S solution was carried out for metal reagent of ZnO and it was found that ZnO can be converted to ZnS, but the conversion was much slower than in the case of $Cu(OH)_2$. Further, the conversion was found to be dependent on S:L ratio used as well as on the pH value of the reacting system. Therefore, the conversion results obtained for ZnO were verified using zinc simulated plating sludge. Finally, the experiments were also carried out for a real plating sludge with high content of zinc in order to confirm the formation of ZnS.

In the case of simulated sludge, the initial molar ratio of S^{2-} to Zn^{2+} was set at 1.50 and the solid to liquid (S:L) ratio was varied from 0.25:50 to 1.00:50. Meanwhile, in the case of real sludge, the S:L ratio was fixed at 1.00:50 and the initial molar ratio of S^{2-} to Me^{2+} (Me stands for all metals present in the sludge) was varied from 1.00 to 1.50. The conversion of zinc compounds to zinc sulfide was evaluated by measuring the residual concentrations of sulfide ions. Further, the formation of zinc sulfide was analyzed using X-ray powder diffraction (XRD) and scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS). In addition, an attempt was made to describe the sulfidation characteristics of zinc compounds involved in the zinc simulated plating sludge by using Elovich kinetic model [2-5].

4.2 Experimental part

4.2.1 Preparation of zinc plating sludge

4.2.1.1 Simulated zinc plating sludge

Figure 4.1 (a) shows the flow chart used for the preparation of simulated zinc plating sludge. An amount of 14.5 g $ZnSO_4 \cdot 7H_2O$ was dissolved in a 400 mL distilled water, and then the pH value of the solution was increased to 9.40±0.10 using 1M

NaOH aqueous solution making up the total volume to 500 mL. The pH value of 9.40±0.10 was chosen with respect to neutralization conditions generally used in the treatment of mixed-metal wastewater streams to lower heavy metal solubilities below the permissible limits [6]. According to Eq.(4.1), zinc ions reacts with hydroxyl ions to form insoluble zinc hydroxide.

$$Zn^{2+} + 2OH^{-} \rightleftharpoons Zn(OH)_2(s) \qquad (4.1)$$

In our experiments, the precipitation was allowed to proceed for 30 minutes, and then the slurry/precipitate was filtered using a filter paper with pore size of 1 μm. After the filtration, the precipitate was rinsed in 500 mL distilled water for another 30 minutes at a constant pH value of 9.40±0.10, in order to purify the zinc precipitate. Subsequently, the precipitate was filtered and dried in a muffle furnace at a temperature of 75°C for 24 hours. The dried precipitate was ground in an agate mortar and screened to particle size lower than 75 μm. The precipitate treated in such manner is hereafter referred to as the simulated zinc plating sludge.

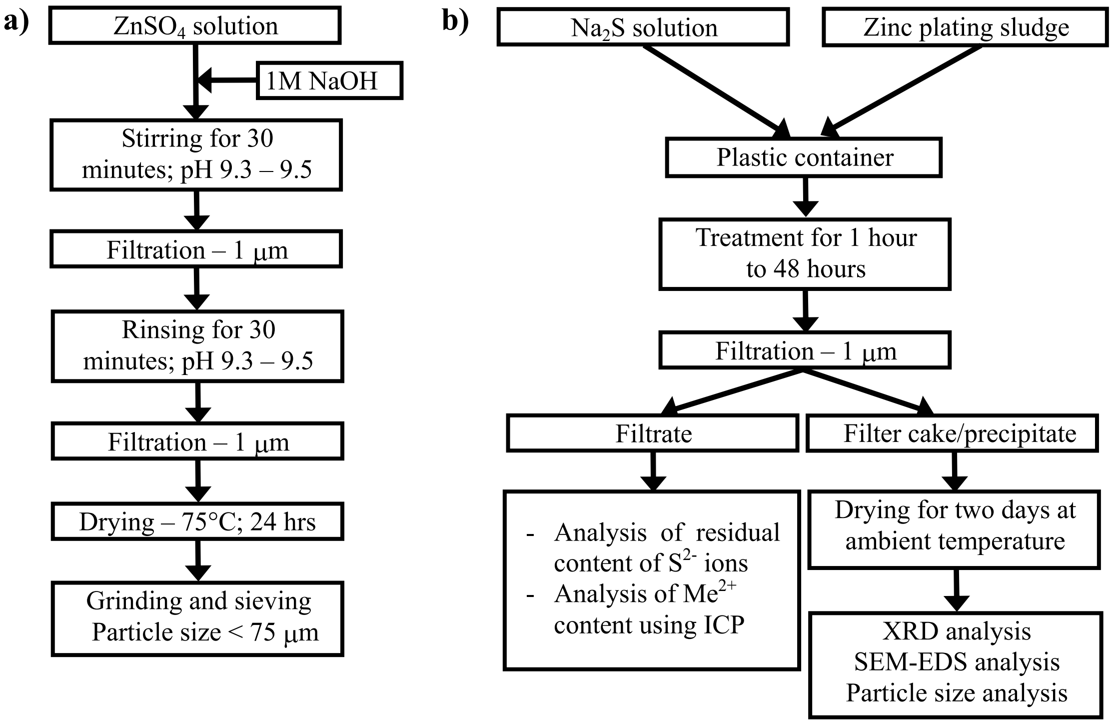


Fig. 4.1: (a) Flow chart of preparation of simulated zinc plating sludge – (b) Flow chart of sulfidation treatment

4.2.1.2 Real plating sludge with high content of zinc

The sample of real plating sludge acquired from Sanshin MFG. Co., Ltd., Japan was used. In a similar way to that of simulated zinc plating sludge, the real plating sludge was dried in a muffle furnace at a temperature of 75°C for 24 hours, and then thoroughly ground and screened using sieves with mesh diameter of 75 μm.

4.2.2 Determination of plating sludge composition

In order to determine the elemental composition of the simulated and real zinc plating sludge, an amount of 100 mg of each sludge was dissolved in aqua regia (a mixture of HCl and HNO_3 at a ratio of 3:1) and the solution arising thereof was analyzed using inductively coupled plasma (ICP) equipment (Vista-MPX Simultaneous ICP-OES, Varian, Inc.). The composition of both plating sludges is given in **Table 4.1**. The average content of zinc in the simulated zinc sludge was found to be 602 mg-Zn/g-sludge. By contrast, the content of zinc in real sludge was only 87.9 mg-Zn/g-sludge, and also other heavy metals such as Cr, Sn etc. were found in the real sludge

Table 4.1: Composition of simulated and real zinc plating sludge

	Simulated sludge Content [mg/g]	Real sludge Content [mg/g]
Zn	602±17.1	87.9±4.82
Cu	-	0.33±0.04
Cd	-	-
Cr	-	61.7±1.90
Fe	-	5.30±0.20
Mn	-	0.29±0.01
Ni	-	2.74±0.05
Pb	-	0.10±0.07
Sn		63.0±1.56
Na	12.2±0.58	7.81±0.35
Ca	-	3.24±0.30
K	-	2.23±0.36

Further, the simulated and real zinc plating sludges were subjected to X-ray powder diffraction (XRD) analysis with scanning mode of $2\theta/\theta$, under the condition of 50 kV/100 mA (RINT-2500 TTR, Rigaku Model), and to scanning electron microscopy–energy dispersive spectrometric (SEM-EDS) analysis (JSM-6330F-JEOL, JED-2140-JEOL). Finally, the simulated zinc plating sludge was analyzed using TG analyzer (TGA-50, Shimadzu) under N_2-O_2 atmosphere of N_2:80%-O_2:20%, at gas flow rate of 50 mL/min and heating rate of 2°C/min.

4.2.3 Sulfidation of zinc plating sludge

4.2.3.1 Simulated zinc plating sludge

The sulfidation of the simulated zinc plating sludge was conducted in a batch system according to the procedure shown in **Fig. 4.1(b)**, and all experiments were carried out in triplicates. First, a volume of 50 mL of Na_2S aqueous solution, of which the initial molar ratio of S^{2-} to Zn^{2+} was adjusted to 1.50, was poured into the plastic containers. The molar ratio of S^{2-} to Zn^{2+} of 1.50 was chosen in order to keep the S^{2-} ions in excess throughout the whole sulfidation period. Second, the simulated zinc sludge was charged into each plastic container in appropriate amount to achieve the S:L ratio of 0.25:50 (weight concentration of about 5 g/L), 0.50:50 (weight concentration of about 10 g/L) or 1.00:50 (weight concentration of about 20 g/L). Then, the plastic containers were shaken on a vertical shaker for 1 to 48 hours. Finally, at the end of the experiment, the slurry was filtered with a filter paper of 1 μm pore size.

4.2.3.2 Real zinc plating sludge

The sulfidation treatment of real sludge was carried out in the similar way as in the case of simulated zinc plating sludge (**Fig. 4.1(b)**). The solid to liquid (S:L) ratio was set to 1.00:50 (sample weight concentration of about 20 g/L), while the initial molar ratio of S^{2-} to Me^{2+} was adjusted to 1.00, 1.25 or 1.50. In the case of real sludge, the initial molar ratio of S^{2-} to Me^{2+} refers to the sum of all heavy metals present in the real sludge (**Table 4.1**). Finally, the sulfidation period of 5 minutes to 12 hours was used for the experiments with the real sludge.

4.2.4 Analyses of filtrate and filter cake

The concentration of the residual sulfides in the filtrate of simulated zinc plating sludge was analyzed using an ion chromatography (Shimadzu, electroconductivity detector type: CDD-10Avp) equipped with a column-Tosoh, TSK gel IC-Anion-PW 6837, 50x4.6 mm I.D. Then, the conversion of zinc compounds to zinc sulfide was calculated according to Eq. (4.2)

$$X = \frac{n_{\mathrm{S_a}} - n_{\mathrm{S_b}} - n_{\mathrm{S_c}}}{n_{\mathrm{Zn}}} \qquad (4.2),$$

where X is the conversion [-], n_{Sa} is the initial amount of sulfide ions [mol], n_{Sb} is the amount of sulfide ions consumed during blank experiment [mol], n_{Sc} is the amount of residual sulfide ions [mol], and n_{Zn} is the total amount of Zn involved in plating sludge [mol]. The amount of the sulfide ions, n_{Sb} [mol] consumed by the oxidation of S^{2-} ions to SO_4^{2-} with oxygen present in water (blank experiment) was determined as a difference between the initial amount of sulfide ions (n_{Sa}) and the residual amount of sulfide ions after performing the blank experiment. In this work, the blank experiments were carried out by shaking only the aqueous Na_2S solutions in plastic containers for a period of 1 to 48 hours. The amounts of $Na_2S{\cdot}9H_2O$ dissolved in water to perform the blank experiments were exactly the same as in the case of experiments performed with simulated zinc plating sludge.

In the case of real plating sludge, the concentration of sulfide ions remaining in the filtrates was measured by S^{2-} ions selective electrode (S-125, Ion meter IM-55G, DKK-TOA Corp.). In the measurements of S^{2-} ions residual concentrations, the pH of the sample solution was kept at a value higher than 13.0, in accordance with the standard procedure for the measurement of S^{2-} ions, and then, the ionic strength of the sample solution was adjusted by L-ascorbic acid.

Finally, the filter cakes were dried at an ambient temperature of about 25°C for 2 days, and then subjected to X-Ray powder diffraction (XRD) analysis. In addition, the particle size distribution of raw sludge and sulfidation products was studied by means of a laser scattering particle size distribution analyzer (Horiba LA-920, Horiba Ltd., Tokyo, Japan).

4.3 Results and discussion

4.3.1 Characterization of simulated zinc plating sludge

From the results obtained by XRD and TGA, it was found that $Zn(OH)_2$ was not the main precipitation product formed during the preparation of simulated zinc plating sludge. Instead, the precipitate was mostly composed of various zinc sulfate hydroxide hydrates which are, in this work, denoted by general formula of $[Zn_x(OH)_y{\cdot}(SO_4){\cdot}nH_2O]$. The TGA results showed that crystalline water in the sludge was evaporated in the temperature range of 165ºC to 300ºC and the remaining $ZnSO_4$ was decomposed to ZnO in the temperature range of 670ºC to 780ºC. Based on the weight loss resulting from the decomposition of $ZnSO_4$ to ZnO, the amount of $ZnSO_4$ involved in zinc sulfate hydroxide hydrate was estimated to be about 17 wt%.

The SEM images of the simulated zinc plating sludge taken at different magnifications are shown in **Fig. 4.2**.

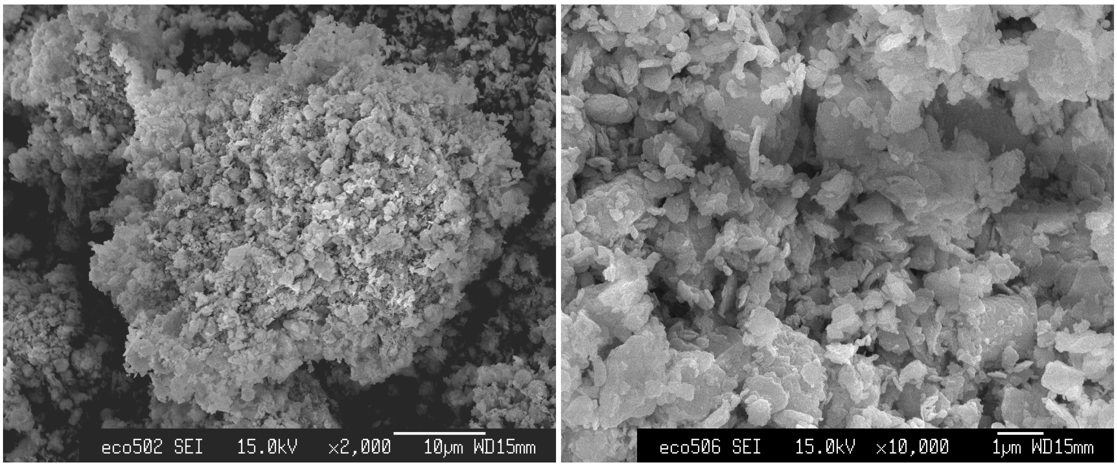


Fig. 4.2: SEM images of simulated zinc plating sludge

As seen in this figure, the particle of zinc plating sludge is an agglomerate of fine floccules of zinc compounds with a diameter of about 1 μm. It is considered that the particles agglomerated during filtration and drying process.

4.3.2 Sulfidation treatment of zinc simulated plating sludge

4.3.2.1 Effect of solid to liquid (S:L) ratio on conversion

The experiments were performed at three different S:L ratios and the results of conversion of Zn compounds to ZnS determined by Eq. (4.2), are plotted against time in **Fig. 4.3**.

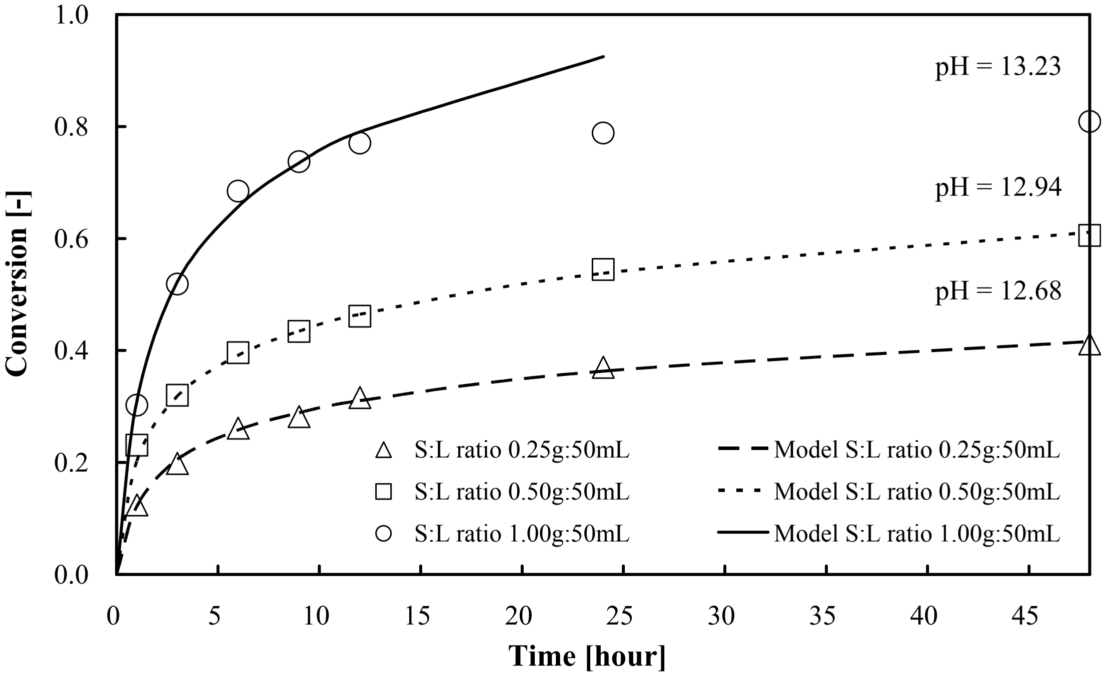


Fig. 4.3: Time plot of conversion of zinc in simulated zinc plating sludge and the results of conversion rate modelling using Elovich kinetic equation

In this figure, the conversion increased rapidly within the first 6 hours for all S:L ratios followed by a slower progress in conversion for the rest of the experimental period. Moreover, the progress in the conversion seemed to stop after 12 hours at the S:L ratio of 1.00:50, and the maximum conversion obtained after 48 hours was 0.809.

The increase in the S:L ratio was accompanied by an increase in the pH value of the reacting system owing to a higher amount of $Na_2S{\cdot}9H_2O$ dissolved in water to establish the given molar ratio of S^{2-} to Zn^{2+} of 1.50. Hence, higher values of the conversion at higher S:L ratios were partially attributed to a higher pH value of the reacting system. The significance of pH arises from an increase in the solubility of Zn compounds with an increase in pH, owing to the formation of more soluble zincates, according to Eqs. (4.3) and (4.4) [7].

$$Zn^{2+} + 3OH^- \leftrightharpoons Zn(OH)_3^- \tag{4.3}$$

$$Zn^{2+} + 4OH^- \leftrightharpoons Zn(OH)_4^{2-} \tag{4.4}$$

Based on the increase in conversion of zinc compounds to ZnS with an increase in pH of the reacting system, it is considered that the solubility of zinc compounds is influential in the sulfidation of Zn compounds to ZnS in the simulated zinc plating sludge. On the contrary, the precipitation of Zn^{2+} ions as insoluble ZnS according to Eqs. (4.5)-(4.7) is supposed to be instantaneous and thus having negligible effect on reaction rate. Such a conclusion is supported by the measurements of zinc concentrations in the filtrates, during which it was found that the zinc concentrations in all filtrates measured by ICP were less than 1 mg/L.

$$Zn^{2+} + S^{2-} \leftrightharpoons ZnS(s) \tag{4.5}$$

$$Zn(OH)_3^- + S^{2-} \leftrightharpoons ZnS(s) + 3OH^- \tag{4.6}$$

$$Zn(OH)_4^{2-} + S^{2-} \leftrightharpoons ZnS(s) + 4OH^- \tag{4.7}$$

4.3.2.2 Analyses of treated zinc plating sludge

After the sulfidation treatment, the simulated zinc plating sludge was subjected to XRD analysis and the XRD patterns obtained are shown in **Fig. 4.4**.

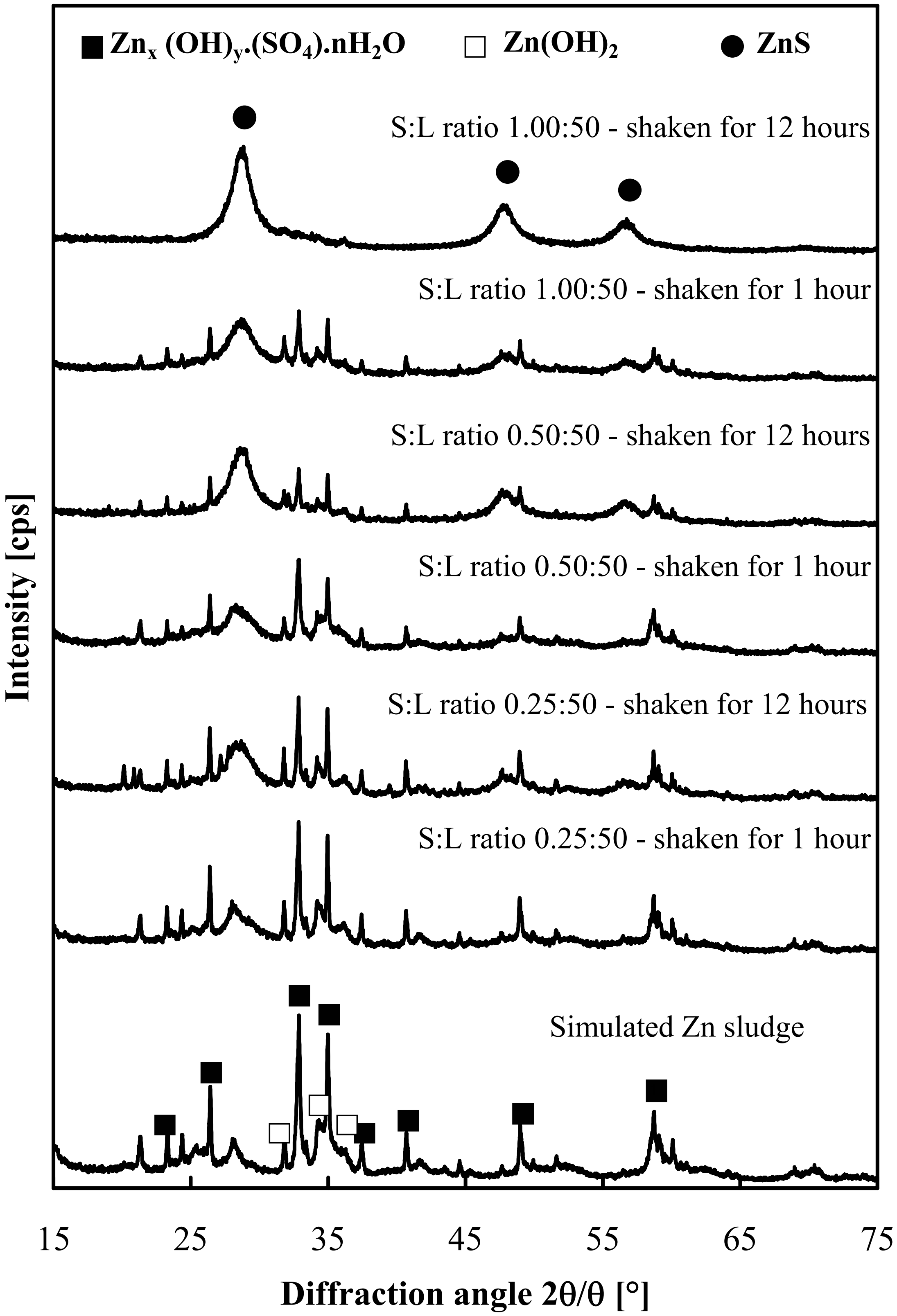


Fig. 4.4: XRD patterns of simulated zinc plating sludge before and after sulfidation treatment

It was confirmed that ZnS was formed as a product of sulfidation of zinc compounds. As indicated in the XRD diagram, characteristic zinc sulfide peak became higher with an increase in sulfidation time as well as with an increase in S:L ratio. It can be observed that only ZnS was present, when the sample was contacted with Na_2S solution for 12 hours at S:L ratio of 1.00:50. Based on the XRD results and the results of conversion (**Fig. 4.3**), it was concluded that a part of the unreacted zinc hydroxide and zinc sulfate hydroxide hydrate was enclosed inside the agglomerates of ZnS.

Figure 4.5 shows the SEM-EDS results of the zinc sludge treated with Na_2S for 12 hours at the S:L ratio of 1.00:50. .

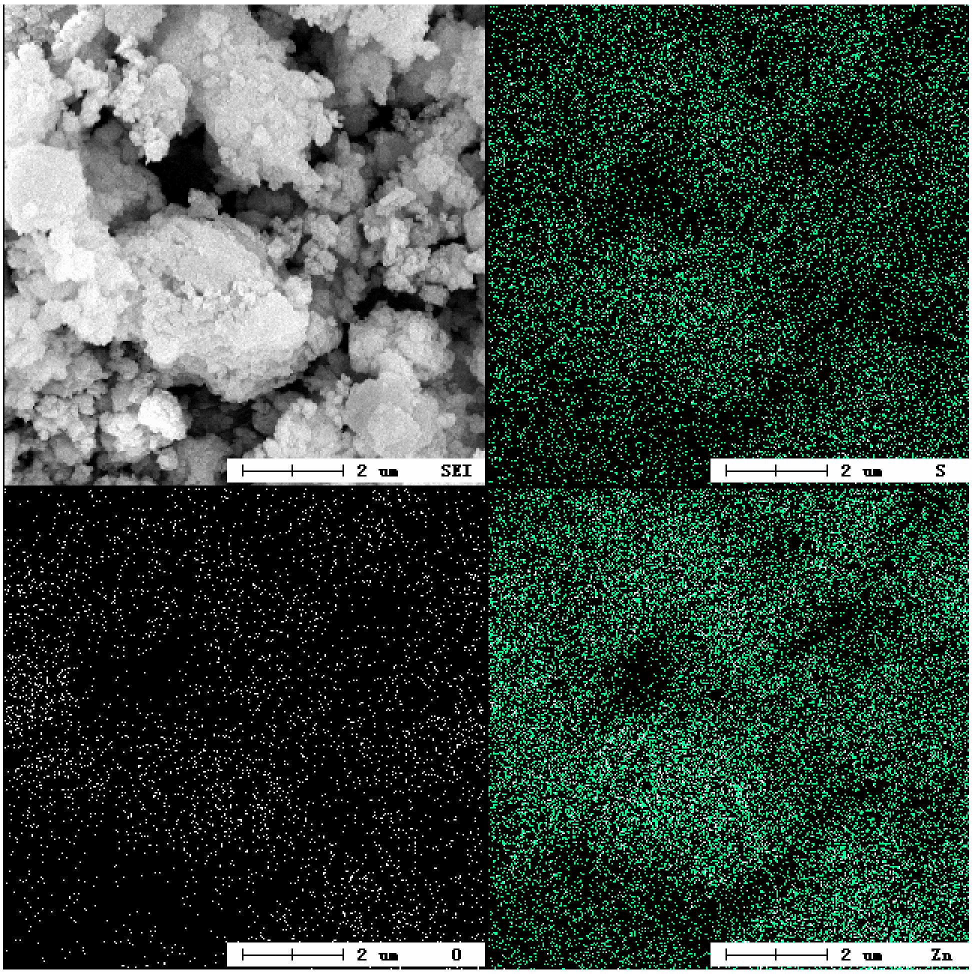


Fig. 4.5: SEM-EDS images of treated simulated zinc plating sludge

From the SEM image, it can be seen that the sulfidation product is composed of fine particles of ZnS. Further, the EDS maps show that zinc, sulfur and oxygen atoms are located at a nearly the same positions, but the number of oxygen atoms detected is significantly lower than those of zinc and sulfur. This result may support the above-mentioned conclusion that some unreacted zinc hydroxide or zinc sulfate hydroxide hydrate was enclosed inside the agglomerates of ZnS.

To conclude this part, it is supposed that the agglomerates of ZnS enclosing unreacted zinc plating sludge should be separable by flotation, since the flotation is based on the surface interactions of particles with flotation agents. Thus, the proposed sulfidation treatment followed by flotation could be used to selectively recover zinc from mixed plating sludges.

4.3.2.3 Evaluation of controlling factors for sulfidation of zinc compounds

As mentioned in Section 4.3.2.1, the conversion of zinc compounds involved in plating sludge to zinc sulfide increased with an increase in S:L ratio and with an increase in the pH value of the reacting system. It is therefore important to evaluate the effect of these two parameters on the sulfidation of zinc compounds. For this aim, the zinc simulated plating sludge was treated with Na_2S solution for 24 hours at a constant S:L ratio of 0.25:50, while the pH value was adjusted with 1M NaOH in the range of 12.68 (without NaOH addition) to 13.30.

Figure 4.6 shows the change in the conversion of zinc compounds involved in plating sludge obtained at the fixed S:L ratio of 0.25:50, while changing pH of the reacting system with NaOH (dashed line). In this figure, the conversions obtained at the S:L ratios of 0.25:50, 0.50:50 and 1.00:50 after 24 hours are also plotted against the pH value of the reacting systems (solid line). In the latter case, the increase in pH value naturally resulted from an increase in the amount of $Na_2S{\cdot}9H_2O$ dissolved in distilled water to adjust the molar ratio of S^{2-} to Zn^{2+} to 1.50 for each S:L ratio and no pH adjustment was made.

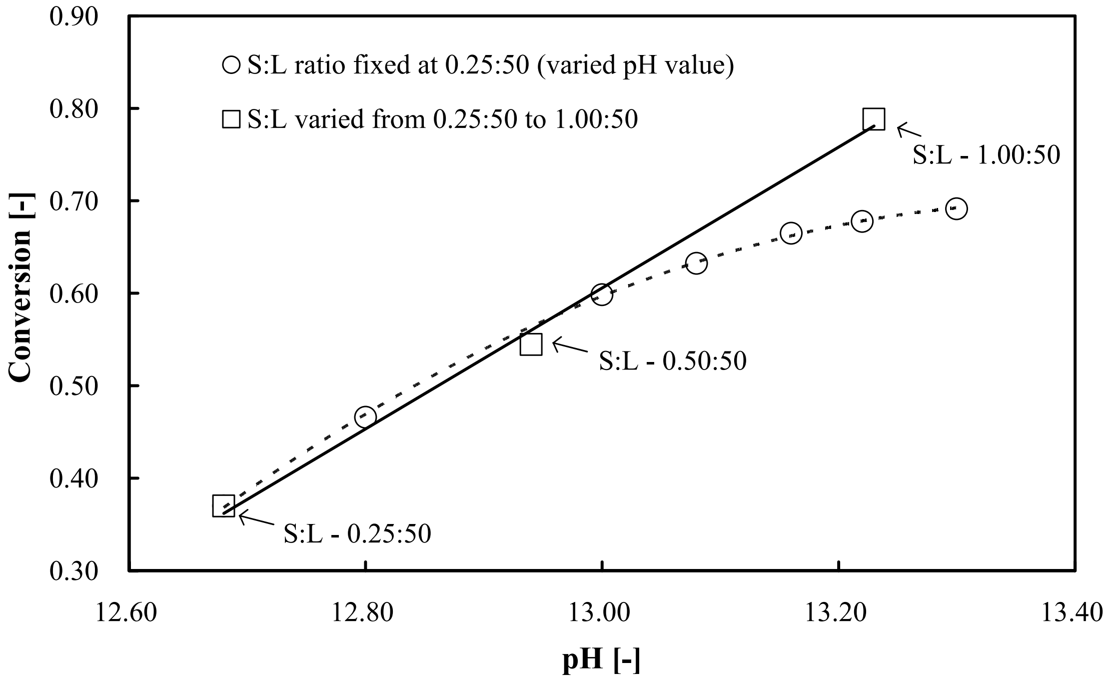


Fig. 4.6: Dependence of conversion on pH value of reacting system

It is shown that the conversion increased linearly with an increase in the pH value resulting from an increase in S:L ratio (solid line). On the contrary, a two stage behaviour was observed when the pH value was adjusted with 1M NaOH at fixed S:L ratio of 0.25:50 (dashed line). In the first stage (pH range of 12.68 to 13.00), the conversion increased almost linearly with an increase in pH, which corresponded to the results obtained when S:L ratio was varied. This result suggested that at an S:L range of 0.25:50 to about 0.50:50, the pH of the reacting system was the main controlling factor, while the effect of change in S:L ratio on the conversion was almost negligible. Then, in the second stage (pH range of 13.00 to 13.30) lower values of conversion were obtained at fixed S:L ratio of 0.25:50 compared to the results obtained when varying S:L ratio (solid line). The result indicated the importance of S:L ratio on the conversion of zinc compounds to ZnS at an S:L ratio higher than 0.50:50.

The S:L ratio is related to the weight concentration of the zinc plating sludge in the reacting system and thus to the number of solid particles in the reacting system. It is assumed that the higher number of particles present in the same volume of the reacting system led to a higher number of mutual collisions of sludge particles at the

S:L ratio of 1.00:50 compared to the number of mutual collisions at the S:L ratio of 0.25:50. Consequently, the agglomerates of raw zinc sludge (**Fig. 4.2**) as well as ZnS agglomerates, in which unreacted zinc compounds were enclosed, disintegrated. Hence, the conversion of zinc compounds to zinc sulfide at a higher S:L ratio became higher, compared to that obtained at a lower S:L ratio and at the same pH value.

In further investigation of this phenomenon, a particle size distribution analysis of the raw simulated zinc plating sludge and the sulfidation products was performed. **Figure 4.7** shows the particle size distribution of raw simulated zinc plating sludge measured by laser scattering particle size distribution analyzer. The particle size distribution analyzer is equipped with ultrasound irradiation used to disintegrate the particle agglomerates. The ultrasound irradiation is directly applied to the sample in the measurement cell and the time duration of ultrasound irradiation is an adjustable parameter (basically the ultrasound irradiation should be applied until a stable particle size distribution is achieved).

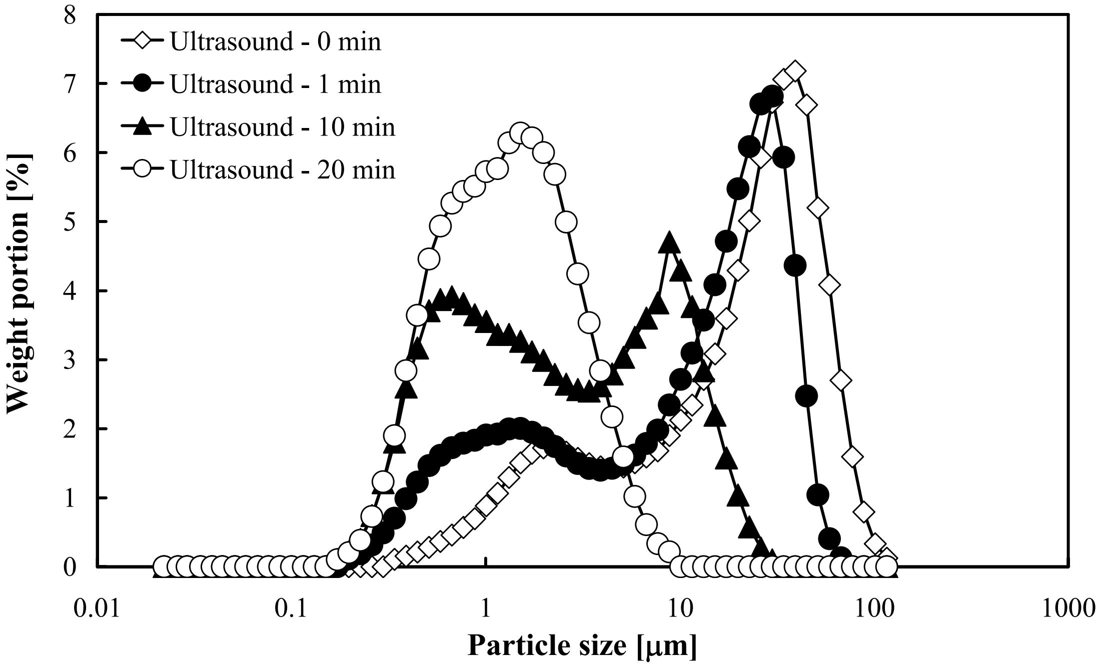


Fig. 4.7: Disintegration of agglomerates of raw zinc simulated sludge with ultrasound irradiation

It can be seen that the particle size distribution of raw sludge prepared by grounding and screening to particle size lower than 75 μm (without ultrasound) showed the highest peak at a particle diameter of about 40 μm and the median of the distribution was 21.84 μm. Then, when ultrasound irradiation was applied, the particle agglomerates were easily disintegrated and the median of distribution obtained after applying the ultrasound irradiation for 20 minutes was 1.20 μm. Thus, based on this analysis, the original particle of raw sludge (particle size lower than 75 μm) are supposed to readily disintegrate during the sulfidation treatment and the disintegration is assumed to increase with an increase in S:L ratio.

After the sulfidation treatment, the sulfidation products obtained by contacting the simulated zinc sludge with Na_2S for 24 hours at S:L ratio of 0.25:50 and 1.00:50 were subjected to particle size distribution analysis and the results are given in **Fig. 4.8**. The results showed that the particle size slightly decreased with an increase in S:L ratio, which is in agreement with our conclusions drawn on the effect of S:L ratio on disintegration of ZnS agglomerates.

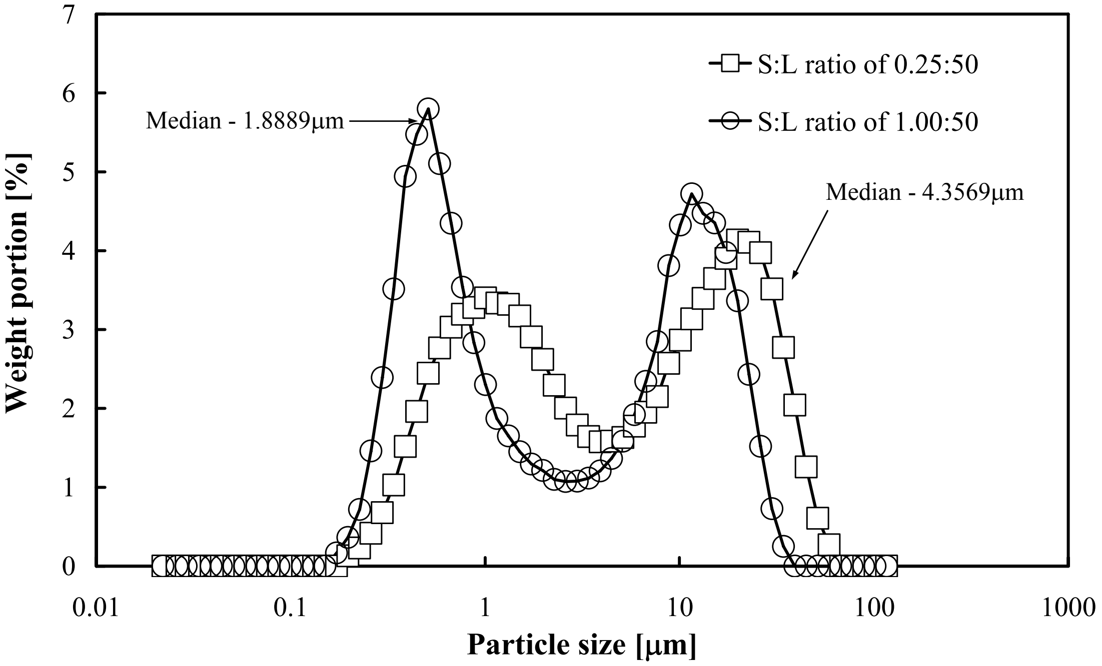


Fig. 4.8: Particle size distribution of sulfidation products obtained after 24 hours at different S:L ratios

4.3.2.4 Modelling of the sulfidation of zinc plating sludge

The conversion of Zn compounds in the plating sludge to ZnS was described using the Elovich kinetic model, which has already been applied in modelling of adsorption of gases on solid adsorbents [2], removal of copper and zinc from effluents [3], extraction of arsenic from contaminated soils [4] and the thermal decomposition of solid oxygenated complexes formed by coal oxidation [5]. The Elovich equation is an empirical model which in terms of the conversion is expressed by Eq. (4.8),

$$\frac{\mathrm{d}X}{\mathrm{d}t} = ae^{-bX} \qquad (4.8),$$

where X is the conversion [-], t is the time [hour] and a, b are the constants – Elovich parameters. The integration of Eq.(4.8) with the boundary conditions of X=0 at t=0, X=X at t=t gives Eq. (4.9).

$$X = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_o) \qquad (4.9)$$

where t_o is the Elovich time constant [hour].

The relation between the conversion X and ln(t+to) obtained from Eq. (4.9) is shown in **Fig. 4.9** for different S:L ratios. The Elovich constants a and b were obtained from the slope and the intercept of the linear regression plot of X against ln(t+to). The constants a and b correspond to the initial reaction rate and the extent of conversion, respectively. In **Fig. 4.10**, the Elovich constants a and b were plotted against S:L ratio. The constant b decreased with an increase in S:L ratio due to a higher conversion ratio achieved at higher S:L ratios. The higher value of the constant a at a higher S:L ratio is attributed to an increase in solubility of zinc compounds in the sludge due to a higher pH value of the reacting system.

The conversion-time curves obtained according to Eq.(4.9) are given in **Fig. 4.3**, in which the solid-, dotted- and dashed-lines are those calculated for S:L ratio of 1.00:50, 0.50:50 and 0.25:50, respectively. The Elovich equation describes the data points fairly well.

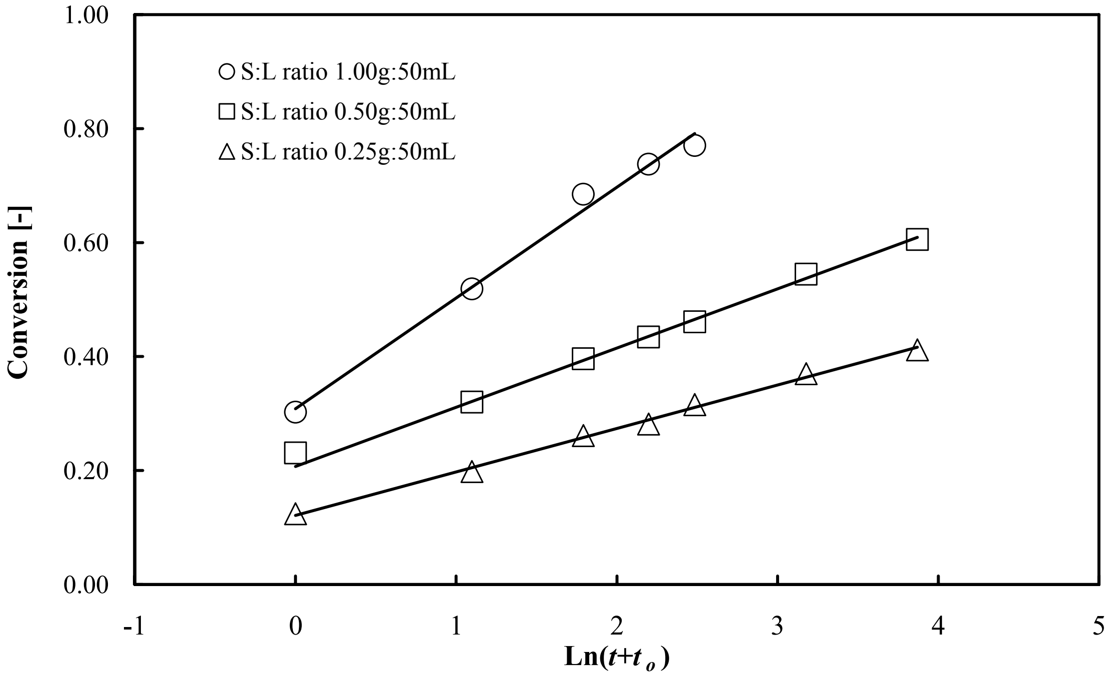


Fig. 4.9: Dependence of conversion on Ln(t+t_o) – Elovich kinetic equation

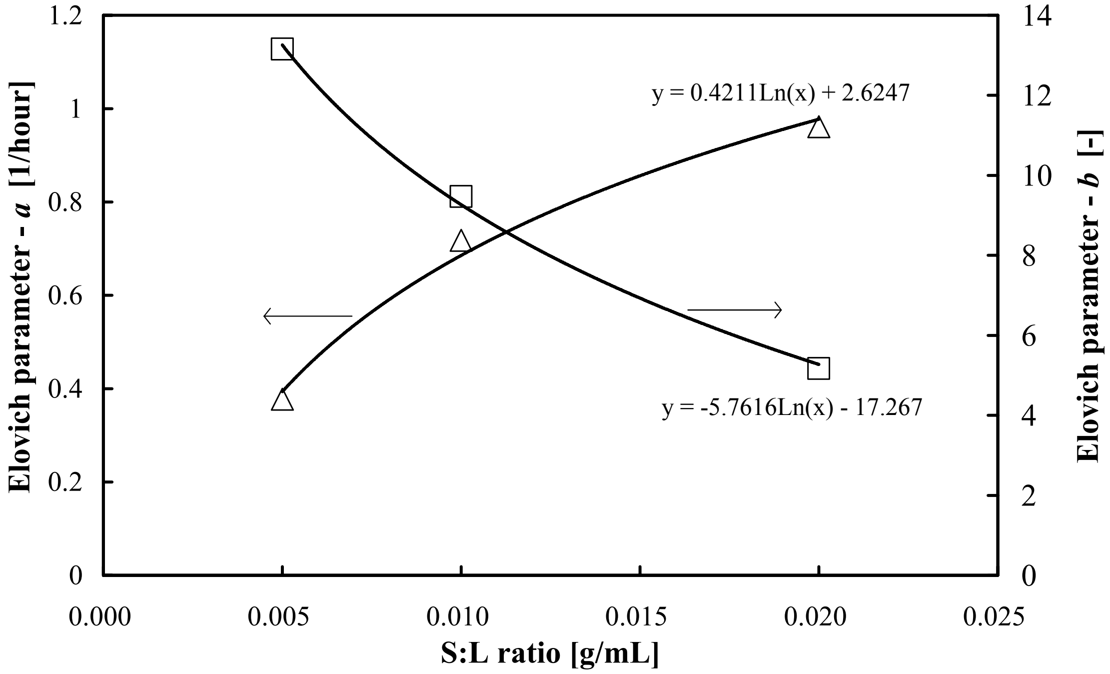


Fig. 4.10: Correlation of Elovich parameters *a* and *b*

In **Table 4.2**, the experimental data on the conversion of zinc compounds in the sludge were compared with those obtained from Eq. (4.9). For this purpose, S:L ratios of 0.375:50 and 0.75:50 were used and the reaction time was set at 3, 12 or 48 hours. It can be seen from **Table 4.2** that the experimental data of the conversion (X_{exp}) were in good agreement with those determined by Elovich kinetic equation (X_{calc}) for the reaction time of 3, 12 and 48 hours, except for S:L ratio of 0.75:50 after 48 hours. It is supposed that at S:L ratio higher than 0.50:50, the sulfidation reaction almost stopped after 12 hours, since the unreacted zinc compounds had been enclosed inside the agglomerates of ZnS.

Table 4.2: Comparison of conversion predicted by Elovich kinetic equation and experimentally obtained conversion

	S:L ratio – 0.375:50		S:L ratio – 0.75:50	
Sulfidation time [hour]	X_{calc} [-]	X_{exp} [-]	X_{calc} [-]	X_{exp} [-]
3	0.266	0.253	0.416	0.404
12	0.394	0.405	0.618	0.597
48	0.521	0.542	0.820	0.684

4.3.3 Sulfidation treatment of real zinc plating sludge

To confirm the applicability of sulfidation treatment to real plating sludges, the experiments were performed for a real sludge with high content of zinc as shown in **Table 4.1**. Similarly as in the case of real copper plating sludge (Chapter 3), the S:L ratio was fixed at 1.00:50 and the initial S^{2-} to Me^{2+} molar ratios of 1.00, 1.25 and 1.50 were used. **Figure 4.11** shows the residual concentrations of sulfide ions measured by S^{2-} ions selective electrode. At first, the residual concentrations of S^{2-} ions rapidly decreased within the first 5 minutes, irrespective of S^{2-} to Me^{2+} molar ratio. Then, within the sulfidation period of 5 minutes to 3 hours, a slower decrease in the residual concentrations of sulfide ions was observed and a stable value was obtained after 3 hours. The conversions obtained after 3 hours were roughly estimated to be 77.2%, 78.3% and 88.0% at S^{2-} to Me^{2+} molar ratios of 1.00, 1.25 and 1.50, respectively (the conversion was calculated based on the sum of molar amounts of all heavy metals).

The increase in S^{2-} to Me^{2+} molar ratio was accompanied by an increase in pH of the reacting system from 12.1 to 12.4 owing to a higher amount of $Na_2S{\cdot}9H_2O$ dissolved in distilled water. Thus, these conversion results are in agreement with the previously described data for ZnO (Chapter 2) and simulated zinc sludge (in this chapter).

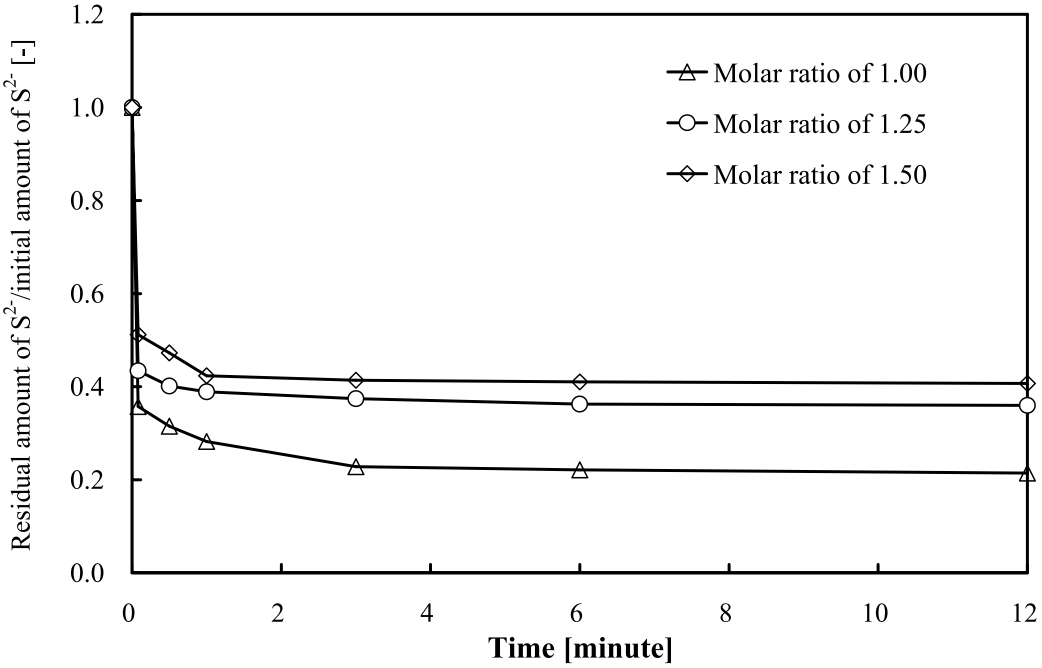


Fig. 4.11: Dependence of residual concentration of S^{2-} ions on time for real plating sludge

Further, the sulfidation products were subjected to an XRD analysis and the XRD patterns obtained are depicted in **Fig. 4.12**. At first, it can be seen that no peaks of heavy metals were identified in the raw plating sludge indicating low crystallinity of metal compounds in the real sludge, which is in agreement with the results obtained for real copper plating sludge (**Fig. 3.8**). Then, when the sulfidation products were analyzed, the peaks of ZnS were clearly identified confirming the conversion of Zn compounds to ZnS.

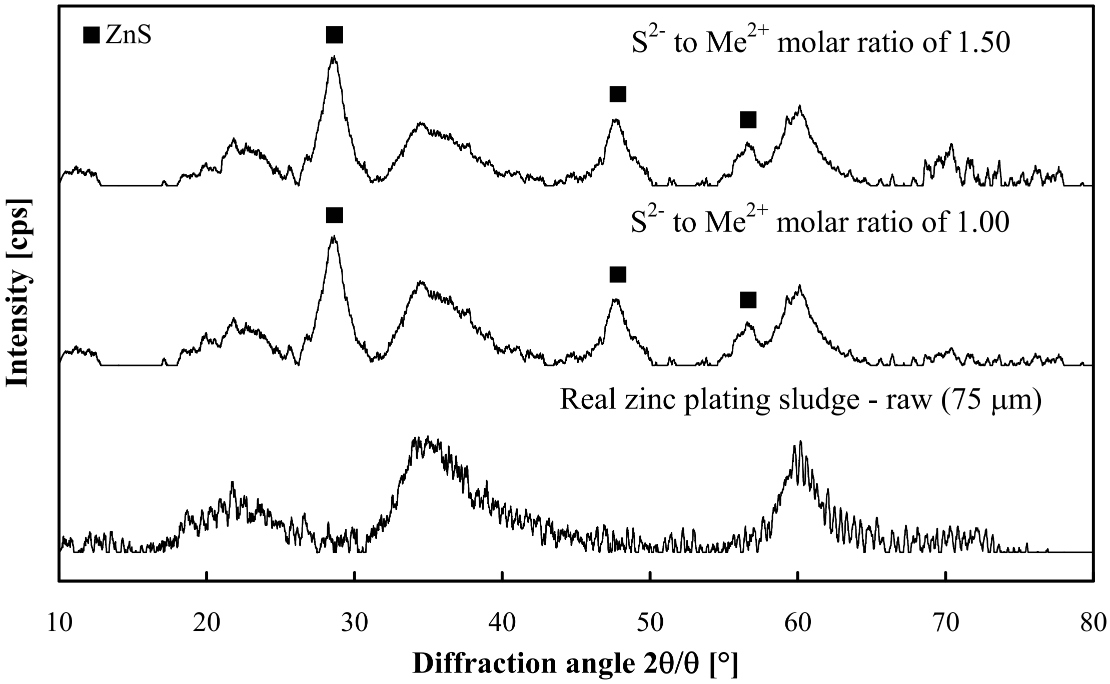


Fig. 4.12: XRD patterns of sulfidation products of real plating sludge obtained after 1 hour at different S^{2-} to Me^{2+} molar ratios

4.4 Conclusions

The sulfidation treatment of simulated zinc plating sludge and real plating sludge with high content of zinc was conducted using Na_2S as a sulfidation agent. As a result, the following conclusions were drawn:

Simulated plating sludge:

In the case of simulated zinc plating sludge, the molar ratio of S^{2-} to Zn^{2+} was fixed at 1.50, while the solid to liquid ratio was varied from 0.25:50 to 1.00:50.

- The XRD analysis of the simulated zinc plating sludge showed that simulated zinc plating sludge was mainly composed of zinc sulfate hydroxide hydrates. Using the thermogravimetric analysis, the amount of unreacted $ZnSO_4$ remaining in zinc sulfate hydroxide hydrates was estimated to be about 17 wt%.

- The conversion of zinc compounds to ZnS increased with an increase in S:L ratio as well as pH value, where the latter resulted from a higher amount of $Na_2S{\cdot}9H_2O$ added to adjust S^{2-} to Zn^{2+} molar ratio for a given S:L ratio. The maximum conversion of 80.9% was obtained at the S:L ratio of 1.00:50 after sulfidation period of 48 hours.

- After the sulfidation for 48 hours at S:L ratio of 1.00:50, only ZnS was detected in the treated zinc sludge using XRD, and thus it is assumed that a part of unreacted zinc sludge remained enclosed in the agglomerates of ZnS. Nevertheless, from the resource recovery point of view, the particles of ZnS enclosing unreacted sludge are supposed to be separable by flotation, and thus, the proposed treatment could be used to selectively recover zinc from mixed plating sludges.

- The sulfidation of zinc compounds in zinc sludge was described by Elovich kinetic equation. It was found that Elovich kinetic model fitted well our experimental data and was further validated at the S:L ratios of 0.375:50 and 0.75:50.

Real plating sludge:

In the case of real plating sludge, the solid to liquid (S:L) ratio was fixed at 1.00:50, while the molar ratio of S^{2-} to Me^{2+} was changed from 1.00 to 1.50.

- The residual concentrations of sulfide ions steeply decreased within the first 5 minutes of sulfidation period indicating high initial conversion rate, and then, the conversion slowly proceeded to attain a minimum value after sulfidation period of 3 hours. The conversions were roughly estimated to be 77.2%, 78.3% and 88.0% at S^{2-} to Me^{2+} molar ratios of 1.00, 1.25 and 1.50, respectively.

- Further, the sulfidation products were subjected to XRD analysis and the formation of zinc sulfide was confirmed, but no other peaks of heavy metal sulfides were identified.

4.5 Nomenclature

a	Elovich parameter [1/hour]
b	Elovich parameter [-]
n_{Sa}	initial amount of sulfide [mol]
n_{Sb}	amount of sulfide ions consumed during blank experiment [mol]
n_{Sc}	amount of residual sulfide ions [mol]
n_{Zn}	total amount of Zn involved in simulated Zn sludge [mol]
t	time [hour]
t_o	Elovich time constant [hour]
X	conversion [-]
X_{calc}	conversion obtained from Elovich kinetic equation [-]
X_{exp}	conversion obtained from experiments [-]

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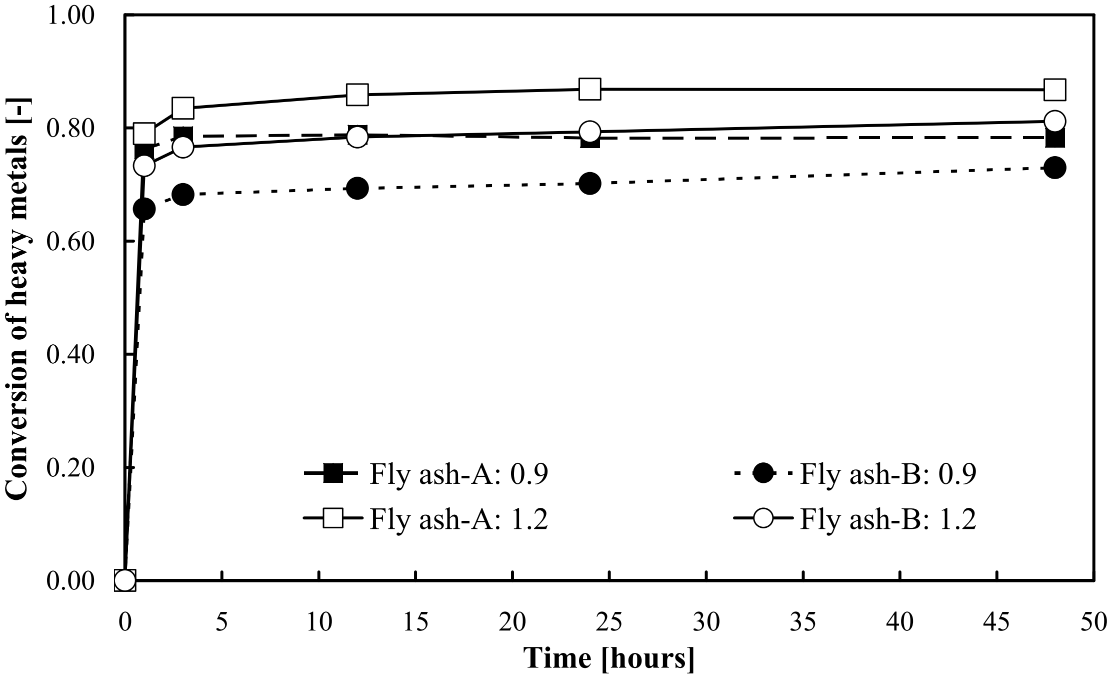
CHAPTER 5

Fundamental study on the sulfidation of molten incineration fly ashes



In this chapter, the sulfidation treatment of molten incineration fly ashes containing heavy metals such as lead, zinc and copper was conducted using Na_2S solution as a sulfidation agent. As a result, the conversions of heavy metals of Pb, Zn and Cu involved in fly ash to metal sulfides obtained after 48 hours at S^{2-} to Me^{2+} initial molar ratio of 1.2 were 86.7% and 81.2% for the molten incineration fly ashes from municipal waste incineration unit and industrial waste incineration unit, respectively.

5.1 Introduction

In Japan, more than 70% of the municipal solid waste produced annually is incinerated to decrease its volume [1], and the incineration residues (bottom ash and fly ash) represent 7-20 wt% of the original waste [2]. Presently, the incineration residues are mainly stabilized/solidified with hydraulic binders [3], asphalt emulsion [4] or glass [5] and then disposed to a landfill site. However, the incineration residues contain valuable heavy metals such as zinc, lead and copper at elevated concentrations. Okada *et al.* [6] reported that the content of zinc in the molten incineration fly ashes varied in the range of 0.27 to 42.5%, the content of lead in the range of 0.13 to 9.2% and the content of copper in the range of 0.11 to 1.6%. As a comparison, the presently mined natural ores contain only about 1-10% zinc, 1-5% lead [7] and 0.5-1.0% copper [8,9]. Thus, from the viewpoint of heavy metal content, the molten incineration fly ashes are considered to be equivalent to the natural ores. Further, it has been reported that the heavy metal resources of lead, zinc, and copper would be depleted in 43 years, 46 years and 61 years, respectively [10]. Therefore, the recovery of heavy metals from various industrial wastes including molten incineration fly ashes should be studied in order to achieve an environmentally friendly society.

For the heavy metal recovery from fly ash, various extraction techniques using mainly an acidic medium have been investigated [11,12]. After the extraction treatment, the heavy metals can be precipitated as metal sulfides, hydroxides, carbonates or chelates. Katsuura *et al.* [11] reported that, among the above mentioned precipitation techniques; the precipitation of heavy metals as heavy metal sulfides was comparatively better in terms of processing properties and cost. However, the precipitation of metal sulfides at pH range of 6.0 to 8.0 required various safety measures to prevent generation of poisonous H_2S gas. Subsequently, the precipitate composed of metal sulfides could be subjected to heavy metal refining process at smelters.

Considering heavy metal recovery at smelters, it should be noted that heavy metals in the nature are present as sulfide ores such as galena (PbS), sphalerite (ZnS) or covellite (CuS). Prior to the smelting, the enrichment of heavy metals by means of flotation technique is carried out [13]. Given this, it is considered that the heavy metals involved in molten incineration fly ash may be directly converted to metal sulfides by mixing a fly ash with an aqueous solution of Na_2S. Subsequently, the fly ash treated with Na_2S in such a manner may be subjected to separation of heavy metal sulfides by means of a flotation. Consequently, in the sulfidation treatment with Na_2S, the acid extraction pre-treatment and the possible generation of H_2S gas in the heavy metal precipitation step could be avoided.

The objective of this study was to investigate the conditions of effective conversion of heavy metals involved in fly ash to heavy metal sulfides, with Na_2S solution. An optimal molar ratio of S^{2-} to Me^{2+} (Me stands for Pb, Zn and Cu) was determined by monitoring the concentrations of heavy metals dissolved in the filtrates. The conversion of heavy metals to the metal sulfides was evaluated by determining the amount of sulfide ions consumed after contacting the fly ash with Na_2S for 1 to 48 hours at S^{2-} to Me^{2+} initial molar ratio of 0.9 and 1.2.

5.2 Experimental part

5.2.1 Elemental composition of molten incineration fly ashes

Two molten incineration fly ashes from municipal and industrial waste incineration units were used in this study. The municipal waste incineration fly ash discharged from gasification and ash melting process, with $Ca(OH)_2$ injection, was denoted as Fly ash-A. Fly ash from gasification and ash melting incineration process of automobile shredder residues, with injection of $Ca(OH)_2$, was denoted as Fly ash-B. **Table 5.1** gives the elemental composition of both fly ashes.

Solubility of heavy metals was evaluated by water leaching test; an amount of 10 g fly ash was charged into plastic container and 100 mL of distilled water was added. The plastic container was placed on a mechanical shaker and shaken vertically at amplitude of 5 cm and a speed of 350 spm for 3 hours. After shaking, the slurry was filtered with a 1 μm pore size filter paper and the concentration of heavy metals in the filtrate was measured by ICP (Vista-MPX Simultaneous ICP-OES, Varian, Inc.).

Table 5.1: Fly ash elemental composition

	Fly ash-A	Fly ash-B
Element	Concentration [mg/g]	Concentration [mg/g]
Zn	20.0	28.0
Pb	16.0	20.0
Cu	2.70	3.80
Fe	0.80	11.2
Cd	0.12	-
Si	1.20	37.4
Al	0.40	7.9
Ca	130	194
Na	166	54.2
K	77.0	68.9
Cl	268	220

The amount of soluble compounds that originally existed in raw fly ash was determined as follows; an amount of 10 g fly ash was shaken with 100 mL distilled water for 24 hours, and the suspension was subsequently filtered. A volume of 10 mL of filtrate was transferred onto a Petri dish, and was heated in a muffle furnace at 105°C to evaporate water. The constant weight of the solid residues after water evaporation corresponded to the amount of water soluble salts involved in fly ash.

5.2.2 Sulfidation treatment

All experiments carried out in a batch system were performed in triplicate and **Figure 5.1** shows the experimental procedure used in the present study. An amount of 10 g fly ash weighed with an accuracy of ± 0.01 g was charged into plastic container. Then, distilled water and an aqueous solution of Na_2S ($Na_2S{\cdot}9H_2O$, Wako Pure Chemical Industries, Ltd.) were added to the container to adjust a solid to liquid (S:L) ratio of 1:10. The S^{2-} to Me^{2+} molar ratio (Me stands for Pb, Zn and Cu) was varied in the range from 0.15 to 1.5. The plastic container was shaken on a vertical shaker for 3 hours at a speed of 350 spm and finally, the slurry was filtered using a 1 μm pore size filter paper. The procedure used was almost the same as that used in the experiments given in previous chapters, with only exception of adding Na_2S aqueous solution and additional distilled water separately. This difference resulted from much lower content of heavy metals in fly ashes than in plating sludges and thus from a significantly lower weight of $Na_2S\cdot9H_2O$ used (especially for the small S^{2-} to Me^{2+} molar ratios such as 0.15 and 0.30). Therefore, to avoid an experimental error during handling small amounts of $Na_2S\cdot9H_2O$, a stock solution of Na_2S was prepared in advance and this solution was later diluted with distilled water to achieve the S^{2-} to Me^{2+} molar ratio of 0.15 to 1.5

When the effect of sulfidation time on the formation of heavy metal sulfides was investigated, the amounts of $Na_2S\cdot9H_2O$ corresponding to the molar ratios of 0.9 and 1.2 were dissolved in 100 mL distilled water (the same procedure as in previous chapters). The Na_2S aqueous solution, prepared in such a manner, was poured into the fly ash charged container to adjust S:L ratio to 1:10 and no distilled water was added. Then, the plastic container was shaken on a vertical shaker for a period of 1 to 48 hours. Finally, the slurry was filtered using a 1 μm pore size filter paper.

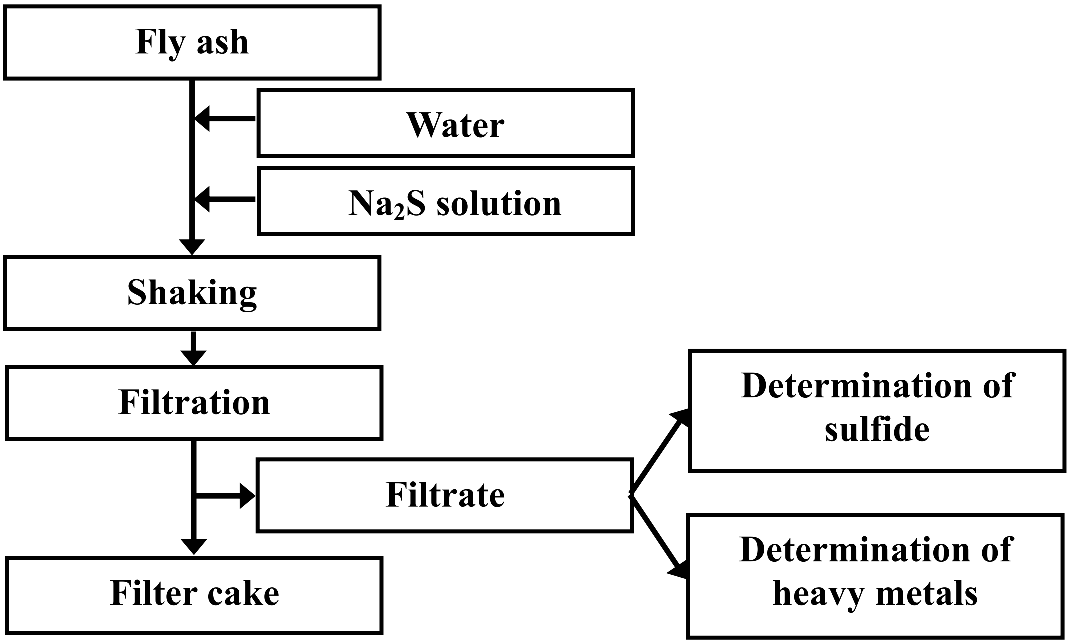


Fig. 5.1: Flow chart of experimental procedure

5.2.3 Analyses of filtrate

The filtrates were subjected to the quantitative analysis of heavy metal content using ICP. The residual concentration of sulfide ions in the filtrates was measured by S^{2-} ions selective electrode (Ion meter IM-55G, DKK-TOA Corp.). Before the actual measurements of S^{2-} ions concentration, the pH of sample solutions was increased to a value higher than 13.0, in accordance with the standard procedure for the measurement of S^{2-} ions with this electrode and the ionic strength was adjusted using L-ascorbic acid.

5.3 Results and discussion

5.3.1 Effect of S^{2-} to Me^{2+} molar ratio on metal concentrations in filtrates

The content of heavy metals in the leachate is shown in **Table 5.2**. The pH values of water leachates of Fly ash-A and Fly ash-B were 12.5 and 12.6, respectively. Among the heavy metals, lead showed the highest concentration at such high pH values, which may be attributed to the formation of soluble Pb compounds such as plumbates [$Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$]. Low concentrations of zinc and copper might have resulted from lower solubility of copper and zinc at such high pH values.

Table 5.2: Concentrations of heavy metals in water leachate

	Fly ash-A	Fly ash-B
Element	Concentration [mg/L]	Concentration [mg/L]
Zn	5.11	7.59
Pb	405	657
Cu	1.22	4.27
Fe	-	-
Cd	-	-

An optimal molar ratio S^{2-} to Me^{2+} was determined by monitoring the concentrations of these metals in filtrates, after sulfidation treatment for 3 hours. In this experiment, S^{2-} to Me^{2+} molar ratio was varied from 0.15 to 1.5. The heavy metals of Pb, Zn and Cu are present in fly ashes in the form of chlorides and oxides [14].

These heavy metals (represented by Me) are considered to dissolve in distilled water according to Eqs. (5.1) and (5.2) and react with S^{2-} ions of Na_2S solution according to Eq. (5.3) to form metallic sulfide.

$$MeCl_2(s) \leftrightharpoons Me^{2+} + 2Cl^- \tag{5.1}$$

$$MeO(s) + H_2O \leftrightharpoons Me^{2+} + 2OH^- \tag{5.2}$$

$$Me^{2+} + S^{2-} \leftrightharpoons MeS \tag{5.3}$$

Figure 5.2 shows the effect of S^{2-} to Me^{2+} molar ratio on the concentration of Pb in the filtrate determined after 3 hours of sulfidation treatment, and it can be seen that the content of Pb in the filtrate decreased as the S^{2-} to Me^{2+} molar ratio increased.

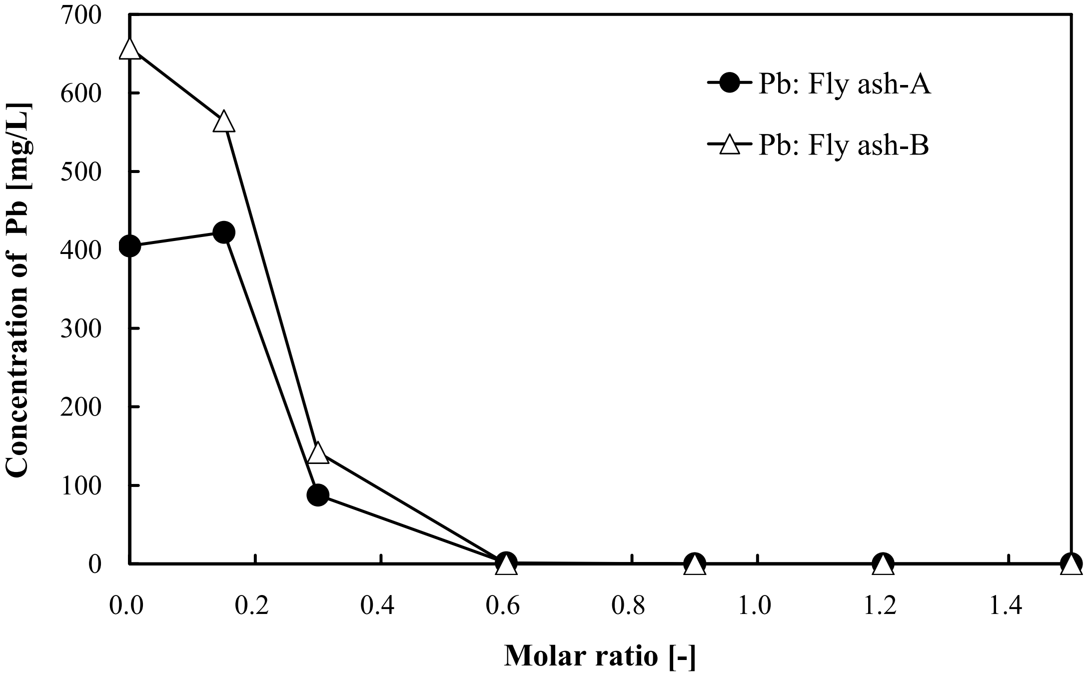


Fig. 5.2: Relation between Pb concentration in filtrate and S^{2-} to Me^{2+} molar ratio

When Na_2S was added to fly ash/water suspension, Pb compounds dissolved in water reacted with S^{2-} according to Eq. (5.3) forming PbS as the reaction product. The decrease in Pb concentration in filtrates with an increase in S^{2-} to Me^{2+} molar ratio suggested that highly soluble Pb compounds were converted to PbS. A slight increase in Pb concentration in the filtrate of Fly ash-A at the S^{2-} to Me^{2+} molar ratio of 0.15 may be attributed to the formation of fine particles of PbS. It is supposed that sulfide ions were consumed almost instantaneously to form fine particles of PbS. When the concentration of sulfide ions was insufficient, these fine particles of PbS could not continue to grow, and consequently easily passed through a 1.0 μm pore size filter. As the S^{2-} to Me^{2+} molar ratio increased, bigger particles of PbS were formed and these particles were effectively separated by filtration. When the S^{2-} to Me^{2+} molar ratio was higher than 0.9, the concentration of Pb in filtrates was lower than 0.1 mg/L.

Figure 5.3 shows the dependence of concentration of Zn and Cu in the filtrate on the S^{2-} to Me^{2+} molar ratio.

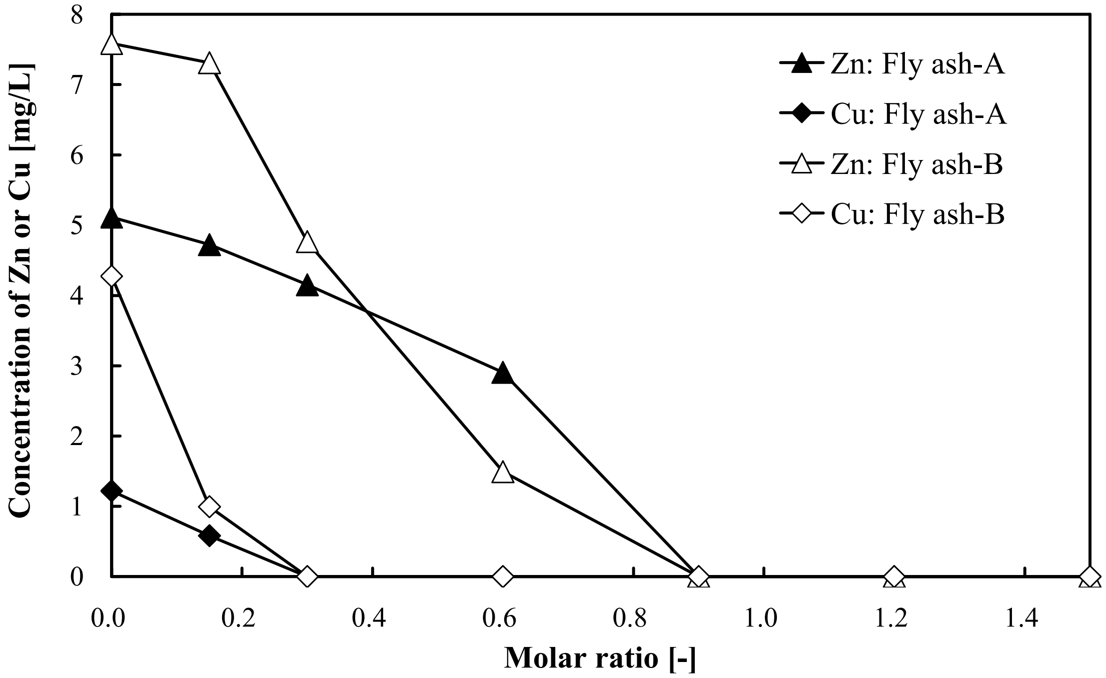


Fig. 5.3: Relation between Cu and Zn concentration in filtrate and S^{2-} to Me^{2+} molar ratio

Similar to the results shown in **Fig. 5.2**, the concentrations of Zn and Cu in the filtrate decreased with an increase in S^{2-} to Me^{2+} molar ratio, and were kept below 0.1 mg/L, when the S^{2-} to Me^{2+} molar ratio was higher than 0.3 and 0.9 for Zn and Cu, respectively. Based on these results, it was concluded that the particles of the ZnS and CuS precipitate were large enough to be separated by a 1.0 μm pore size filter.

The low values of heavy metal concentrations in filtrates at S^{2-} to Me^{2+} molar ratio higher than 0.3 for Cu and higher than 0.9 for Pb and Zn suggested that all easily soluble heavy metals were precipitated as heavy metal sulfides. In addition, the concentration of sulfide ions in the reaction solution was considered to be high enough to keep the dissolution of less soluble heavy metal oxides and hydroxides at low values.

5.3.2 Effect of sulfidation time on formation of heavy metal sulfides

As mentioned in the introduction, the objective of this work was to convert heavy metals to heavy metals sulfides which could thereafter be recovered by flotation. The conversion of heavy metals to metal sulfides is considered to be a time dependent process and thus cannot be evaluated only by measurements of amounts of metals dissolved in the solution **(Figs. 5.2 and 5.3)**, since the bulk part of metal compounds is assumed to remain un-dissolved. Therefore, the effect of time on the conversion was investigated for both fly ashes at a sulfidation period of 1 to 48 hours. The conversion of heavy metals to sulfides was evaluated by measuring the amounts of sulfide ions consumed at S^{2-} to Me^{2+} molar ratios of 0.9 and 1.2 at each sulfidation time.

When Na_2S is added to fly ash, S^{2-} ions are consumed by the following reactions.

$$Me^{2+} + S^{2-} \leftrightarrows MeS(s) \tag{5.4}$$

$$S^{2-} + 2O_2 \leftrightarrows SO_4^{2-} \tag{5.5}$$

$$S^{2-} + 2H^+ \leftrightarrows H_2S(g) \tag{5.6}$$

Heavy metals are converted to metal sulfides by sulfidation reaction expressed by Eq. (5.4). Equation (5.5) describes the oxidation of S^{2-} ions, which becomes significant when O_2 is present in water. Further, it is likely that H_2S is formed according to Eq. (5.6), when the pH of the solution becomes lower than 9.0, but the formation of H_2S gas was assumed to be negligible in our experiments since the pH values of the reacting systems were kept higher than 12.3.

To estimate the amount of sulfide ions consumed by the reactions expressed by Eqs.(5.5) and (5.6), blank experiments were conducted by dissolving Na_2S in distilled water with no fly ash charged. The amounts $Na_2S{\cdot}9H_2O$ dissolved in distilled water to perform blank experiment corresponded to S^{2-} to Me^{2+} molar ratios of 0.9 and 1.2. The pH of blank solutions of Fly ash-A and Fly ash-B varied from 12.4 to 12.9, corresponding to the amount of $Na_2S{\cdot}9H_2O$ dissolved in distilled water. Subsequently, the conversion of heavy metals to heavy metal sulfides was determined using Eq. (5.7).

$$X = \frac{n_{Sa} - n_{\mathrm{Sb}} - n_{\mathrm{Sc}}}{n_{\mathrm{Me}}} \qquad (5.7),$$

where X is the conversion of heavy metals [-], n_{Sa} is the initial amount of sulfide [mol], n_{Sb} is the amount of sulfide ions consumed during blank experiment [mol], n_{Sc} is the amount of residual sulfide ions [mol], and n_{Me} is the amount of Pb, Zn, Cu in fly ash [mol].

Figure 5.4 shows the relation between the conversion of heavy metals to heavy metal sulfides and sulfidation time at the S^{2-} to Me^{2+} molar ratios of 0.9 and 1.2. As seen from the figure, the conversion increased rapidly within the first 1 hour, and then the conversion continued to proceed at a lower rate to attain a stable value after 24 hours. This trend in conversion might have resulted from complex reactions during sulfidation of different heavy metal compounds. It is considered that highly soluble heavy metal compounds such as chlorides were converted to sulfides within the first 1 hour. Subsequently, the sulfidation of less soluble oxides and hydroxides might have taken place.

The experiments carried out at different S^{2-} to Me^{2+} molar ratios showed that the S^{2-} to Me^{2+} molar ratio of 0.9 was not sufficient for Fly ash-A since the residual sulfide concentration was almost negligible after 3 hours. The conversion achieved after 3 hours at this ratio was 78.5%, while the conversion achieved at the S^{2-} to Me^{2+} molar ratio of 1.2 was 83.5% after sulfidation for 3 hours. The extension of sulfidation time to 48 hours brought about a slight conversion increase to a value of 86.7% at the S^{2-} to Me^{2+} molar ratio of 1.2.

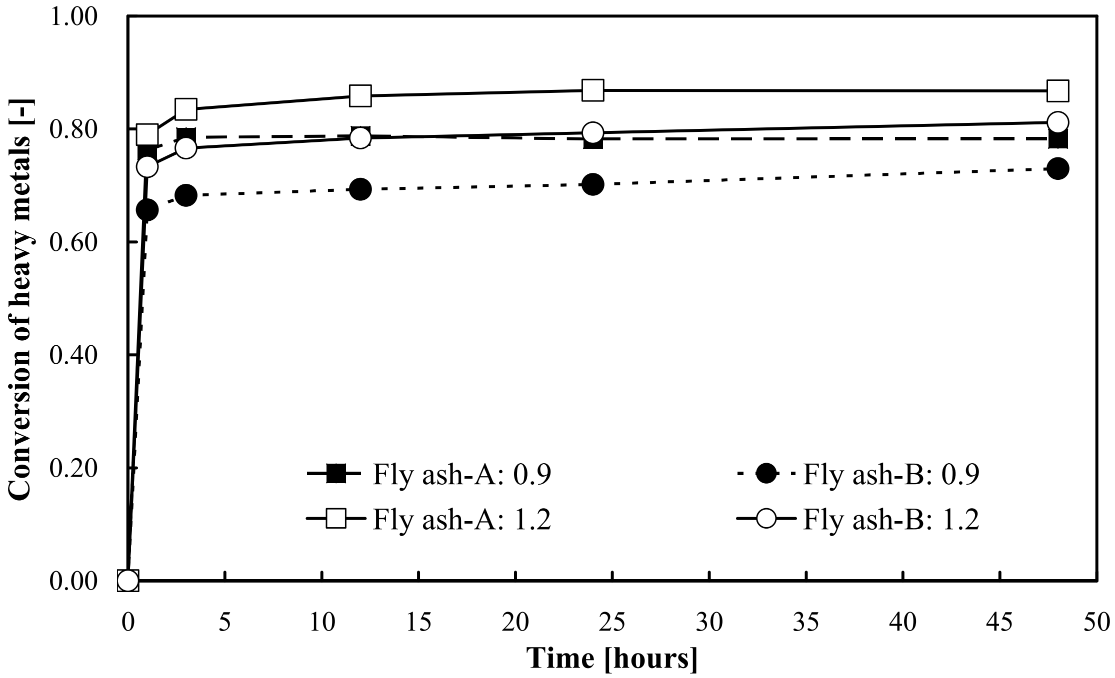


Fig. 5.4: Relation between conversion of heavy metals to metal sulfides and sulfidation time

In the case of Fly ash-B, the conversion achieved at the S^{2-} to Me^{2+} molar ratio of 0.9 was 68.2% even when the concentration of residual sulfides was sufficiently high (200 mg/L), while the conversion increased to a value of about 76.6% at the S^{2-} to Me^{2+} molar ratio of 1.2 after 3 hours. It is considered that lower conversion is attributable to a slightly lower pH value at the S^{2-} to Me^{2+} molar ratio of 0.9 than that of 1.2, since the pH values of filtrates were 12.3 and 12.5 for the S^{2-} to Me^{2+} molar ratios of 0.9 and 1.2, respectively. The maximum conversion achieved was 81.2% after 48 hours at the S^{2-} to Me^{2+} molar ratio of 1.2.

Under our experimental conditions, a complete conversion of heavy metals to heavy metal sulfides was not achieved even after sulfidation time of 48 hours. It is supposed that the rest of unreacted heavy metals may have been incorporated in the lattice of SiO_2 and Al_2O_3 in fly ash and thus unavailable for the reaction with S^{2-} ions.

5.3.3 Content of heavy metals in treated fly ash

Sulfidation treatment is naturally accompanied by removal of soluble salts, which leads to an enrichment of heavy metals in fly ash. Using the procedure described in Section 5.2.1, the total amounts of water soluble salts were determined to be 64.5 wt% for Fly ash-A and 51.1 wt% for Fly ash-B. These soluble salts are principally composed of Na, K, Ca chlorides, besides soluble heavy metal compounds. For a comparison, the total amounts of NaCl, KCl and $CaCl_2$ involved in Fly ash-A and Fly ash-B were also calculated based on the data provided in **Table 5.1** and it was determined that Fly ash-A and Fly ash-B contained 64.1 wt% and 53.7 wt% of water soluble salts, respectively.

Finally, when it is assumed that the removal of soluble salts is not affected by the sulfidation treatment, it can be estimated that the total content of Zn, Pb and Cu in Fly ash-A increased from 3.87 wt% (untreated fly ash) to 10.9 wt%, and from 5.18 wt% to 10.6 wt% in Fly ash-B.

5.4 Conclusions

Two fly ashes from municipal (Fly ash-A) and industrial (Fly ash-B) wastes incineration units were sulfidized with Na_2S aqueous solution to convert heavy metals involved in the fly ashes to heavy metal sulfides. The S^{2-} to Me^{2+} molar ratio was varied from 0.15 to 1.5.

- As a result, 86.7% of heavy metals in Fly ash-A and 81.2% of heavy metals in Fly ash-B were converted to heavy metal sulfides after 48 hours sulfidation at the S^{2-} to Me^{2+} molar ratio of 1.2.
- Furthermore, it was estimated that approximately 64.5 wt% and 51.1 wt% of soluble compounds such as NaCl, KCl and $CaCl_2$ were removed during sulfidation treatment from Fly ash-A and Fly ash-B, respectively.

- The removal of soluble salts brought about an enrichment of heavy metals in fly ash and the heavy metal content was estimated to increase from 3.87 wt% (untreated fly ash) to 10.9 wt% for Fly ash-A, and from 5.18 wt% to 10.6 wt% for Fly ash-B. The major part of heavy metals is considered to be present as metal sulfides which could be recovered from treated fly ashes by means of flotation.

5.5 Nomenclature

n_{Me}	amount of Pb, Zn, Cu in fly ash [mol]
n_{Sa}	initial amount of sulfide [mol]
n_{Sb}	amount of sulfide consumed during blank experiment [mol]
n_{Sc}	amount of residual sulfide [mol]
X	conversion of heavy metals [-]

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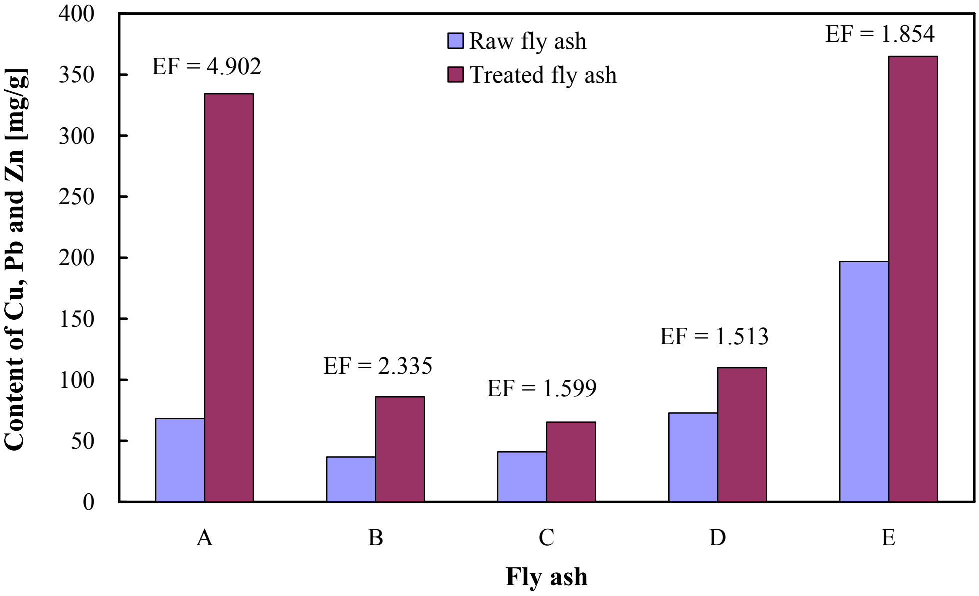
CHAPTER 6

Sulfidation of molten incineration fly ashes: sulfidation characteristics and characterization of sulfidation products



This chapter present the result of thorough study on sulfidation behaviour of five different molten incineration fly ashes (Fly ash-A to Fly ash-E). It was found that, in the case of Fly ash-A to Fly ash-D, more than 79% of heavy metals of zinc, lead and copper was converted to metal sulfides within the contacting period of 0.5 hour, while the conversion of about 35% was achieved for Fly ash-E within the same contacting period. Further, when the S^{2-} to Me^{2+} molar ratio was reduced to 1.00 to minimize Na_2S consumption (experiments performed only for Fly ash-A to Fly ash-D), the conversions obtained within the contacting period of 0.5 hour varied from 76% for Fly ash-D to 91% for Fly ash-C. Finally, soluble salts such as NaCl and KCl were removed during the sulfidation treatment, which brought about a significant enrichment in heavy metals content by a factor varying from 1.5 for Fly ash-D to 4.9 for Fly ash-A.

6.1 Introduction

In this chapter, more elaborated study on the sulfidation behaviour of molten incineration fly ashes containing heavy metals such as Zn, Pb and Cu was carried out. The effect of contacting time on the conversion of heavy metals to metal sulfides was investigated at an initial molar ratio of S^{2-} to Me^{2+} (Me stands for heavy metals of Zn, Pb and Cu) of 1.20. Furthermore, the effect of pH on the conversion of heavy metals to metal sulfides was investigated at a contacting period of 0.5 hour and S^{2-} to Me^{2+} molar ratio of 1.20. In the next experiments, the S^{2-} to Me^{2+} molar ratio was reduced to 1.00 to minimize the consumption of sulfidation agent of Na_2S and the sulfidation treatment was performed at a period of 0.5 hour. The conversion of heavy metals to metal sulfides was evaluated by measuring the residual amount of sulfide ions in the filtrates. Further, as mentioned in Chapter 5, water soluble salts such as NaCl, KCl and $CaCl_2$ were removed from fly ash during the sulfidation treatment which resulted in an enrichment of the heavy metal content. This enrichment was evaluated using an enrichment factor of *EF*. Finally, the sulfidation products were analyzed by means of an X-Ray powder diffraction (XRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS).

6.2 Experimental part

6.2.1 Elemental composition of molten incineration fly ashes

Three molten incineration fly ashes obtained from a municipal waste incineration plant were denoted as Fly ash-A, Fly ash-B and Fly ash-E, while two fly ashes acquired from incineration process of automobile shredder residues were denoted as Fly ash-C and Fly ash-D. Before the experiments, the Fly ash-A, which was received in a wet state, was dried at a temperature of 105°C and then finely ground. The Fly ashes from B to E, which were received in a dry state, were used as received.

6.2.1.1 Determination of elemental composition of fly ashes using ICP-OES

The elemental composition of each fly ash was determined as follows: an amount of 2.0 g of each fly ash was subjected to an ultrasound assisted digestion in a mixture of HCl and HNO_3 at the ratio of 3:1, for two hours. Then, the leachate arising thereof was filtered using a 1 μm pore size filter paper and the elemental composition was analyzed using ICP (Vista-MPX Simultaneous ICP-OES, Varian, Inc.). The analyses of silica and alumina content in the molten incineration fly ashes were not performed since the elemental composition of molten incineration fly ashes has been well reported in the literature, for example Okada *et al.* [1].

6.2.1.2 Determination of chloride content using ion chromatography

The content of chlorides in each fly ash was determined using the following procedure: at first, an amount of 0.5 g of fly ash was subjected to an ultrasound assisted digestion in 10% HNO_3 for 2 hours [1]. Then, the leachate was filtered using a 1 μm pore size filter and the filtrate obtained was analyzed using an ion chromatography (Shimadzu, electroconductivity detector type: CDD-10Avp) equipped with a column-Tosoh, TSK gel IC-Anion-PW 6837, 50x4.6 mm I.D.

6.2.1.3 Determination of crystallographic composition of fly ashes using XRD

Crystallographic composition of molten incineration fly ashes was evaluated using X-Ray powder diffraction (XRD) analysis with scanning mode of $2\theta/\theta$, under the condition of 50 kV/100 mA (XRD; RINT-2500 TTR, Rigaku Model).

6.2.2 Sulfidation treatment

At first, an amount of 10.0 g fly ash weighed with an accuracy of ± 0.01 g was charged into a plastic container. Then, a volume of 100 mL Na_2S aqueous solution

($Na_2S\cdot 9H_2O$, Wako Pure Chemical Industries, Ltd.) used as a sulfidation agent was poured into the container. Based on the results reported in Chapter 5, the sum of the molar amounts of zinc, lead and copper involved in raw fly ashes was used to determine an amount of $Na_2S\cdot 9H_2O$ dissolved in 100 mL distilled water to achieve an initial molar ratio of S^{2-} to Me^{2+} of 1.20 (Me stands for the sum of Zn, Pb and Cu determined in the given fly ash). Subsequently, the plastic container was placed on a vertical shaker and was shaken for a period varying from 10 minutes to 6 hours. At the end of the experiment, the slurry was filtered using a 1 μm pore size filter paper.

6.2.3 Analyses of filtrates and filter cakes

The concentrations of heavy metals in the filtrates were determined by means of an ICP and the residual concentrations of S^{2-} ions were analyzed using an S^{2-} ions selective electrode (S-125, Ion meter IM-55G, DKK-TOA Corp.). Before the measurements of S^{2-} ions, the pH of the sample solution was increased to a value higher than 13.0, in accordance with the standard procedure for the measurement of S^{2-} ions and the ionic strength of the sample solution was adjusted with L-ascorbic acid. The conversion of zinc, lead and copper to metal sulfides was determined using Eq. (6.1).

$$X = \frac{n_{\mathrm{S_a}} - n_{\mathrm{S_b}} - n_{\mathrm{S_c}}}{n_{\mathrm{Me}}} \qquad (6.1),$$

where X is the conversion [-], n_{Sa} is the initial amount of sulfide [mol], n_{Sb} is the amount of sulfide ions consumed during a blank experiment [mol], n_{Sc} is the amount of residual sulfide ions [mol], and n_{Me} is the molar amount of Zn, Pb and Cu involved in a given molten incineration fly ash [mol]. The blank experiments were conducted by shaking only Na_2S aqueous solution in order to determine the consumption of S^{2-} ions by the oxidation reactions.

The filter cakes were dried at an ambient temperature of about 25°C for 2 days, and then subjected to X-Ray powder diffraction (XRD) analysis and to scanning electron microscopy - energy dispersive spectrometric analysis (SEM-EDS; JSM-6330F-JEOL, JED-2140-JEOL).

6.2.4 Enrichment of heavy metals in treated fly ash

The elemental composition of treated fly ashes was analyzed in the same way as that of the raw fly ashes. Subsequently, the enrichment factor, defined as a ratio of the sum of Zn, Pb and Cu in the treated fly ash to the sum of Zn, Pb and Cu in the raw fly ash, was determined using Eq. (6.2),

$$EF = \frac{m_{\text{Me-treated FA}}}{m_{\text{Me-raw FA}}} \qquad (6.2),$$

where EF is the enrichment factor [-], $m_{\text{Me-treated FA}}$ is the total amount of Zn, Pb and Cu in the treated fly ash [mg/g] and $m_{\text{Me-raw FA}}$ is the total amount of Zn, Pb and Cu in the raw fly ash [mg/g].

6.3 Results and discussion

6.3.1 Characterization of molten incineration fly ashes

The composition of each molten incineration fly ash was determined in triplicate and the results are given in **Table 6.1**. As can be seen from this table, the molten incineration fly ashes contained high concentrations of heavy metals such as Zn, Pb and Cu as well as high concentrations of Na, Ca, K and Cl^-. To determine the crystallographic composition, the molten fly ashes were subjected to an XRD analysis as shown in **Fig. 6.1**. From this figure, it can be seen that the main characteristic peaks identified in all molten fly ashes were those of NaCl and KCl. To a smaller extent, characteristic peaks of $CaCO_3$ were found in Fly ash-B and Fly ash-E, but no other peaks of Ca compounds such as $CaCl_2$ or $CaSO_4$ were identified, which is in an agreement with the results reported by Zhang and Itoh [2]. In their work, it was considered that Ca, which is mainly introduced into the fly ash from an external source such as lime used to neutralize the flue acid gas, was mainly present as amorphous $CaCl_2$, $Ca(OH)_2$, CaS, $CaSO_4$, etc.

Table 6.1: Elemental composition of fly ashes

	Fly ash-A (MSW^a)	Fly ash-B (MSW^a)	Fly ash-C (ASR^b)	Fly ash-D (ASR^b)	Fly ash-E (MSW^a)
Element	Content [mg/g]	Content [mg/g]	Content [mg/g]	Content [mg/g]	Content [mg/g]
Zn	55.1±1.06	18.7±0.23	20.7±0.84	54.2±0.67	173±1.6
Pb	10.3±0.57	15.5±0.06	17.2±0.18	16.1±0.22	22.3±0.12
Cu	2.83±0.19	2.59±0.02	2.97±0.09	2.50±0.02	1.11±0.01
Fe	1.61±0.26	0.71±0.06	3.87±0.24	0.95±0.01	11.5±0.55
Sn	1.59±0.04	1.80±0.08	0.74±0.04	1.82±0.02	1.21±0.02
Cd	0.23±0.00	0.09±0.00	0.10±0.00	0.02±0.00	0.15±0.00
Mn	0.03±0.00	-	1.84±0.11	0.04±0.00	0.40±0.03
Cr	0.05±0.02	0.04±0.03	0.03±0.01	0.03±0.00	0.10±0.00
Ni	-	-	-	-	0.02±0.00
Na	167±9.24	162±4.66	39.6±2.01	47.0±0.16	77.6±0.58
Ca	1.39±0.19	144±7.49	219±10.2	336±4.44	72.5±0.54
K	234±4.14	63.8±5.57	71.7±1.70	16.1±0.15	112±2.47
Cl$^-$	538±4.57	439±6.98	378±0.69	363±1.54	374±8.48

[a] MSW – Municipal Solid Waste

[b] ASR – Automobile Shredder Residue

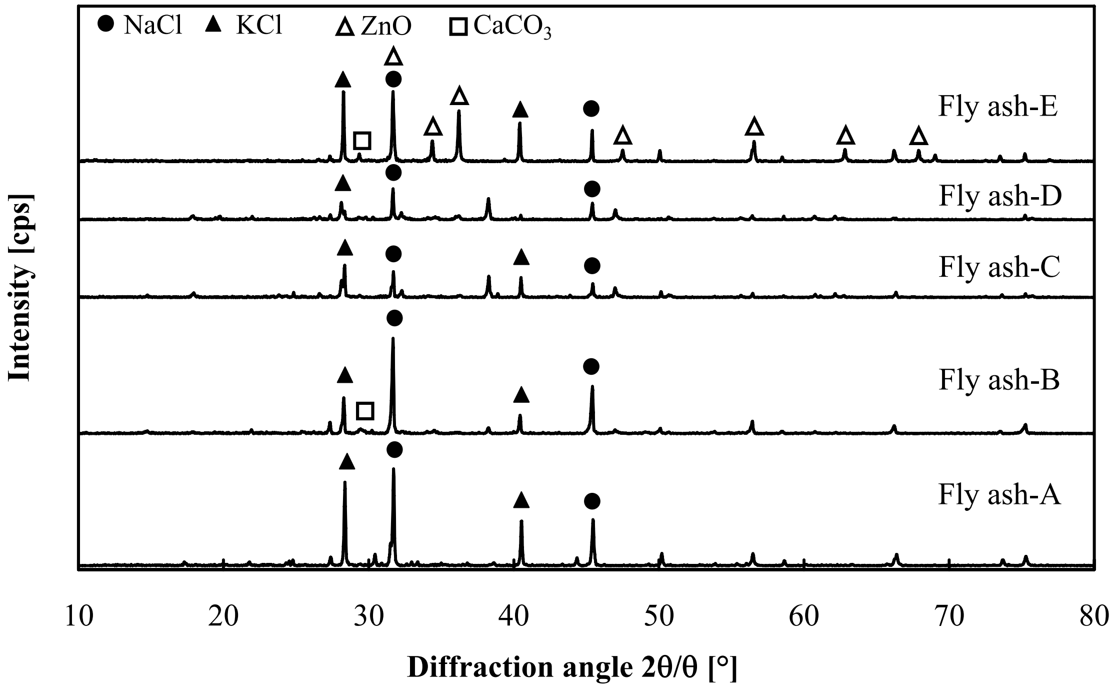


Fig. 6.1: Crystallographic composition of fly ashes

As for the heavy metals, the characteristic peaks of ZnO were identified in Fly ash-E, but no other characteristic peaks of heavy metals were found in Fly ash-A to Fly ash-D. This result suggested that heavy metals were either present in amorphous forms or the amount of a particular chemical form was not high enough to allow the detection by XRD. In the literature, several researchers reported that X-Ray absorption fine structure (XAFS) spectroscopy could be used for the speciation of Pb and Zn involved in fly ashes and it was found that heavy metals were present in fly ashes as metal chlorides, oxides and carbonates [3]. These heavy metal chlorides, oxides and carbonates are supposed to dissolve in water as expressed by Eqs. (6.3) – (6.5). Then, in the sulfidation treatment of these heavy metal compounds, Me^{2+} ions react with S^{2-} ions to form metal sulfides, as expressed by Eq.(6.6).

$$MeCl_2(s) \rightleftharpoons Me^{2+} + 2Cl^- \quad (6.3)$$

$$MeO(s) + H_2O \rightleftharpoons Me^{2+} + 2OH^- \quad (6.4)$$

$$MeCO_3(s) \rightleftharpoons Me^{2+} + CO_3^{2-} \quad (6.5)$$

$$Me^{2+} + S^{2-} \rightleftharpoons MeS(s) \quad (6.6)$$

6.3.2 Effect of contacting period on sulfidation of heavy metals

The effect of contacting period on the conversion of heavy metals of zinc, lead and copper to metal sulfides was investigated for all molten incineration fly ashes. **Figure 6.2** shows the time change of conversion of heavy metals to metals sulfides obtained at a contacting period of 10 minutes to 6 hours for Fly ash-A to Fly ash-E. As seen in the figure, the conversion of heavy metals in the case of molten incineration fly ashes A to D steeply increased within the first 10 minutes of contacting each fly ash with Na_2S solution, which may be attributed to the fast conversion of highly soluble metal chlorides to metal sulfides. Subsequently, when the contacting period was extended up to 6 hours, less soluble heavy metal compounds such as metal oxides were gradually converted to metal sulfides. The conversions of heavy metal compounds to heavy metal sulfides obtained after 6 hours were 1.00±0.02, 0.94±0.02, 0.95±0.01 and

0.86±0.01 for Fly ash-A, Fly ash-B, Fly ash-C and Fly ash-D, respectively. By contrast, the conversion of only 0.21±0.03 was obtained for Fly ash-E within the contacting period of 10 minutes and the conversion slowly increased to a value of 0.65±0.01 at the contacting period of 6 hours. Based on the XRD analysis of Fly ash-E, the low conversion rate obtained for Fly ash-E was attributed to high content of metal oxides, especially ZnO, which are generally characterized by a lower solubility than metal chlorides.

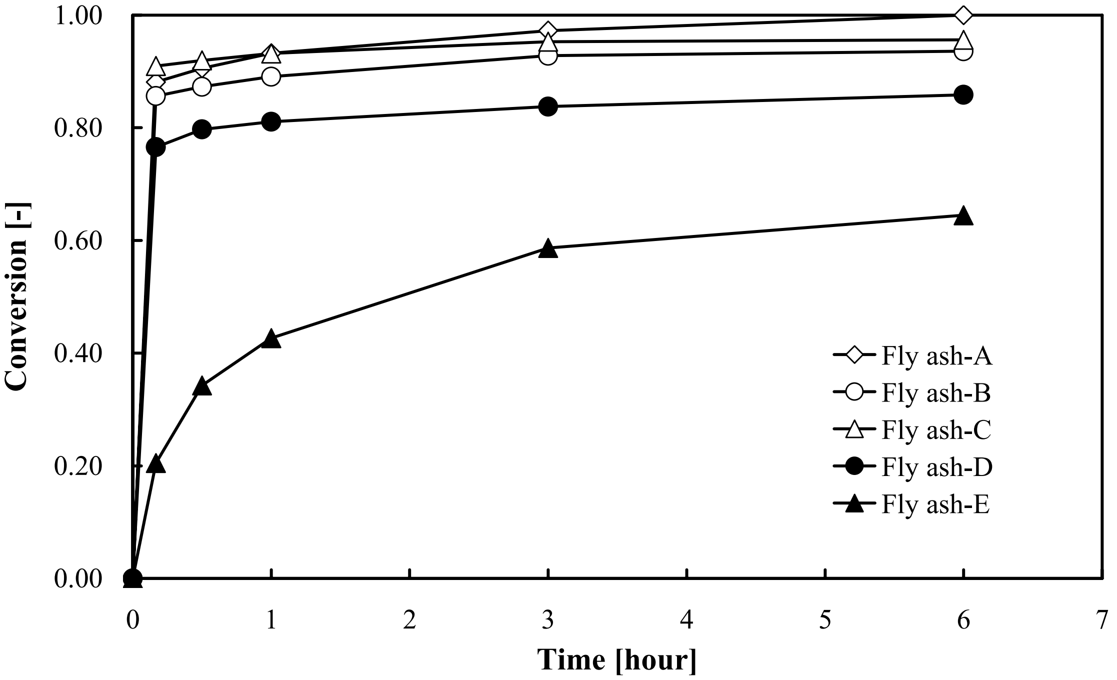


Fig. 6.2: Time change of the conversion of heavy metals to metals sulfides for Fly ash-A to Fly ash-E

As shown in **Table 6.1**, the sum of heavy metals of Zn, Pb and Cu in Fly ash A to E varied from a value of 36.8±0.30 mg/g for Fly ash-B to a value of 196±1.50 mg/g for Fly ash-E. Therefore, an attempt was made to evaluate the relation between the heavy metals content in the raw fly ash and the conversion of heavy metals to metal sulfides. **Figure 6.3** shows the relation between the sum of Zn, Pb and Cu in the raw fly ashes and the conversion obtained at a contacting period of 0.5 hour. In addition, the relation between the Zn content in the fly ashes and the conversion obtained at the same contacting period is shown in this figure, since the highest variation in the content was observed for zinc. In the case of Fly ash-B to Fly ash-E, it can be seen that the conversion almost linearly decreased with an increase in the content of heavy metals. More precisely, it can be seen that the decrease in the conversion mainly resulted from an increase in the content of zinc. As described in Section 6.3.1, the heavy metals are generally present in molten incineration fly ashes as metal chlorides, oxides and carbonates, but the exact proportion of chlorides, oxides and carbonates was not clear for the fly ashes used in this study. However, in accordance with XRD analysis of Fly ash-E, it can be assumed that the amount of less soluble metal oxides, such as zinc oxide, increased with an increase in the total amount of heavy metals, which brought about a lower conversion.

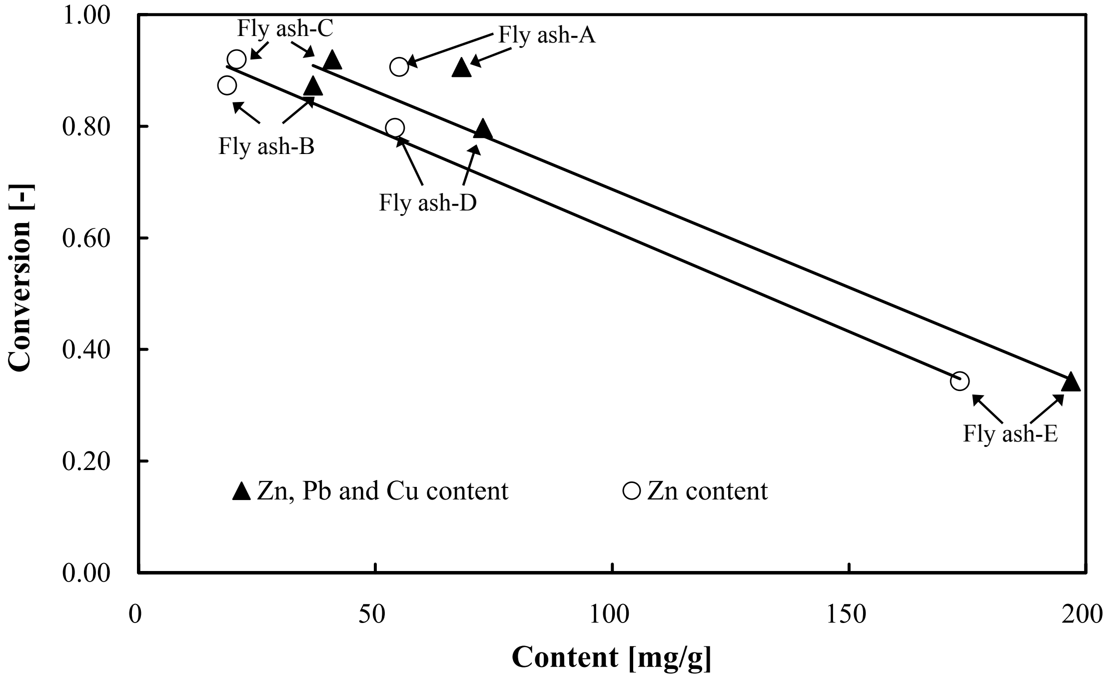


Fig. 6.3: Effect of sum of Zn, Pb and Cu contents and Zn content alone on conversion of heavy metals to metals sulfides for Fly ash-A to Fly ash-E

Furthermore, Nagib and Inoue [4] reported that the leachability of zinc from molten fly was much lower than that of lead in an alkaline pH range. In this study, the sulfidation experiments were conducted at a pH value of about 13.0 and thus the decrease in conversion with an increase in zinc content might also be attributed to a lower solubility of zinc in an alkaline pH range.

Finally, despite almost the same Zn content in Fly ash-A and Fly ash-D, different conversion values were obtained for these two fly ashes. It was considered that, in the case of Fly ash-A, zinc was present mainly as soluble $ZnCl_2$, which brought about a higher conversion than that obtained for Fly ash-D. In fact, a high leachability of zinc from Fly ash-A of 2,620 mg/L was obtained by shaking raw fly ash in distilled water for a period of 0.5 hour at a solid to liquid ratio of 1:10 (10 g fly ash to 100 mL distilled water). On the contrary, the leachability of zinc from Fly ash-B to Fly ash-E varied in the range of 2.17 mg/L for Fly ash-E to 11.77 mg/L for Fly ash-B. Correspondingly, the pH value of the water leachate of Fly ash-A was 6.39, which was significantly lower than the pH values of water leachate of Fly ash-B to Fly ash-E, which were in the range of 11.07 to 12.35.

6.3.3 Effect of pH on sulfidation of heavy metals

In the previous experiments (**Figs. 6.2 and 6.3**), no pH adjustment was made and the pH value of the reacting system resulted from an amount of $Na_2S \cdot 9H_2O$ dissolved in water to establish an initial molar ratio of S^{2-} to Me^{2+} of 1.20 as well as from the presence of alkaline compounds in the given fly ash. In our experiments, the pH values of the reacting systems were determined to be in the range of 12.2 for Fly ash-D to 13.2 for Fly ash-E. Generally, heavy metals of zinc, lead and copper are of amphoteric nature and their solubility is greatly affected by pH value. The lowest solubility of these heavy metals is obtained in a pH range of 9.0 to 10.0, and then the solubility increases with an increase in the pH value owing to the formation of zincate, plumbate and cuprite ions. Therefore, in order to investigate the effect of pH on the conversion of heavy metals to metal sulfides, additional experiments on sulfidation treatment of fly ashes were conducted in an alkaline pH range. The pH value was adjusted by dissolving $Na_2S \cdot 9H_2O$ in distilled water with additions of 5, 10, 20, 30 or 50 mL of 1M NaOH to make up a total volume of 100 mL. The contacting period was set to 0.5 hour and the initial molar ratio of S^{2-} to Me^{2+} was kept at 1.20.

Figure 6.4 shows the relation between the conversion and the pH of the reacting system for all fly ashes used in this study. From this figure, it can be seen that the conversion values obtained for Fly ash-A to Fly ash-D were almost constant in the whole pH range used. By contrast, in the case of Fly ash-E, the conversion increased linearly with an increase in pH. As described in Section 6.3.1, Fly ash-E was characterized by the highest content of zinc among all fly ashes used, and the XRD analysis of Fly ash-E (**Fig. 6.1**) showed that zinc is present in the form of ZnO, while no distinctive peaks of heavy metals were found in other fly ashes. Hence, the low conversion of about 0.35 obtained for Fly ash-E at a contacting period of 0.5 hour and a pH value of 13.2 was attributed to the presence of a significantly higher amount of ZnO in Fly ash-E.

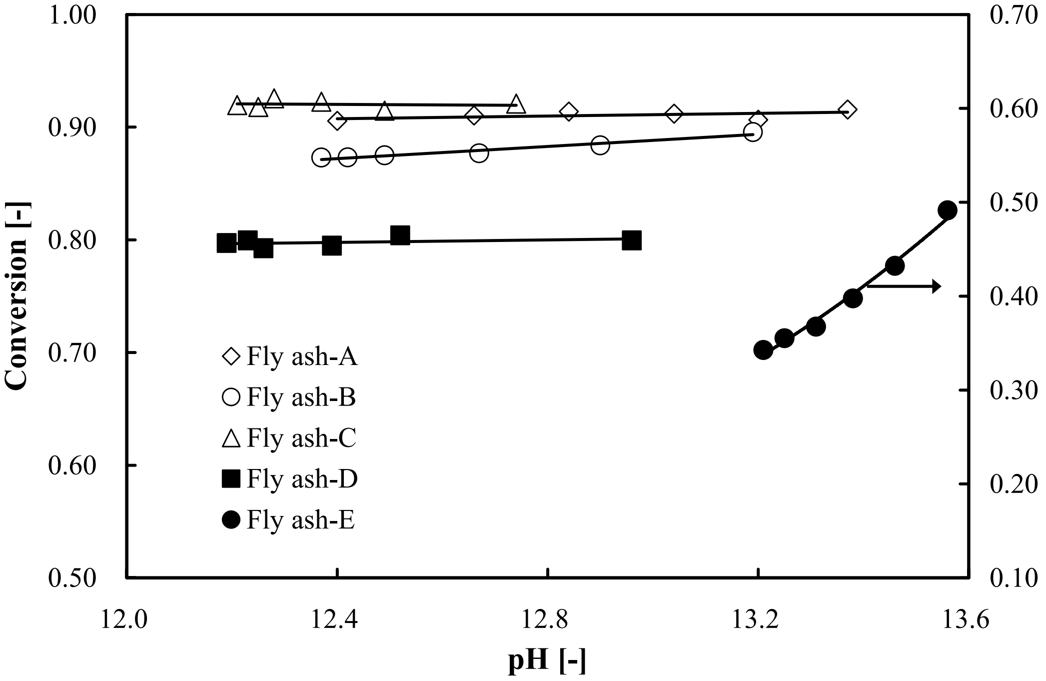


Fig. 6.4: Effect of pH on conversion of heavy metals to metals sulfides for Fly ash-A to Fly ash-E

However, when the pH of the reacting system was increased from a value of 13.2 to a value of 13.6, more soluble zincates were formed as expressed by Eq. (6.7) [5].

$$\mathrm{ZnO}(cr) + \mathrm{H_2O}(l) + x\mathrm{OH}^-(aq) \leftrightarrow \mathrm{Zn(OH)}_{2+x}^{x-}(aq) \tag{6.7}$$

Subsequently, the soluble zincates ions reacted with S^{2-} ions present in the solution to form insoluble ZnS, as expressed by Eqs. (6.8) and (6.9), which led to an increase in the conversion to a value of about 0.49 at a pH value of 13.6, for Fly ash-E.

$$Zn(OH)_3^- + S^{2-} \leftrightharpoons ZnS(s) + 3OH^- \tag{6.8}$$

$$Zn(OH)_4^{2-} + S^{2-} \leftrightharpoons ZnS(s) + 4OH^- \tag{6.9}$$

6.3.4 Optimization of conditions of sulfidation treatment and enrichment factor of heavy metals

The residual concentration of S^{2-} ions determined after 0.5 hour of contacting fly ash with Na_2S varied from 267.6 mg/L for Fly ash-C to 714.6 mg/L for Fly ash-A. Therefore, in the next step, the experiments were conducted for Fly ash-A to Fly ash-D at the S^{2-} to Me^{2+} molar ratio 1.00 to minimize the consumption of sulfidation agent of Na_2S, while the contacting period was kept at 0.5 hour. At the end of the experiment, the heavy metals concentrations in the filtrates of fly ash-Na_2S-water slurry were determined using ICP and the residual concentrations of S^{2-} ions were determined using an S^{2-} ions selective electrode. The heavy metals contents in the treated fly ashes were determined in the same way as the heavy metals contents in raw fly ashes.

Table 6.2 summarizes the main parameters determined by the analyses of filtrates and filter cakes of treated molten incineration fly ashes A, B, C and D. In addition, solely for the purpose of an evaluation of enrichment factor, the Fly ash-E was subjected to leaching in distilled water in a solid to liquid ratio of 1:10 (10 g fly ash to 100 mL distilled water) for 0.5 hour and the corresponding results are also given in **Table 6.2**. At first, it was found that the conversion values obtained for Fly ash-A to Fly ash-D at an initial S^{2-} to Me^{2+} molar ratio of 1.00 were almost the same as those obtained at S^{2-} to Me^{2+} molar ratio of 1.20. Further, it was observed that the contents of Na and K, mainly present in the raw fly ashes as soluble salts such as NaCl and KCl, were remarkably reduced during the sulfidation treatment. Conversely, the content of Ca in the treated fly ashes was higher than that in raw fly ashes, which is in agreement with the assumption that calcium is present in the fly ashes in less soluble chemical forms such as $CaCO_3$, $Ca(OH)_2$, $CaSO_4$ etc. [2].

Table 6.2: Parameters determined by analyses of filtrates and filter cakes

	Fly ash-A	Fly ash-B	Fly ash-C	Fly ash-D	Fly ash-E[a]
Conversion [-]	0.87±0.02	0.85±0.01	0.91±0.00	0.76±0.00	-
Filtrate					
Zn [mg/L]	0.53	0.27	0.15	-	2.17
Pb [mg/L]	-	-	-	-	2.04
Cu [mg/L]	-	-	-	-	0.22
S^{2-} [mg/L]	266	140	124	557	-
Filter cake/Treated molten incineration fly ash					
Zn [mg/g]	270±1.53	43.2±0.38	33.0±0.05	82.7±0.49	320±3.93
Pb [mg/g]	49.4±0.24	36.5±0.66	27.6±0.22	23.4±0.09	43.2±0.27
Cu [mg/g]	14.6±0.17	6.25±0.20	4.88±0.121	3.98±0.01	2.14±0.15
Na [mg/g]	45.9±3.35	15.8±0.66	13.6±0.55	10.8±0.16	15.2±0.06
Ca [mg/g]	9.11±0.02	294±3.42	157±1.70	399±1.86	116±0.92
K [mg/g]	52.4±1.15	7.93±0.22	17.8±0.30	24.1±0.05	13.0±0.01
EF [-]	**4.90**	**2.34**	**1.60**	**1.51**	**1.85**

[a] The sulfidation treatment was not applied to Fly ash-E and the results shown in this table were determined by the analysis of water leachate and corresponding filter cake

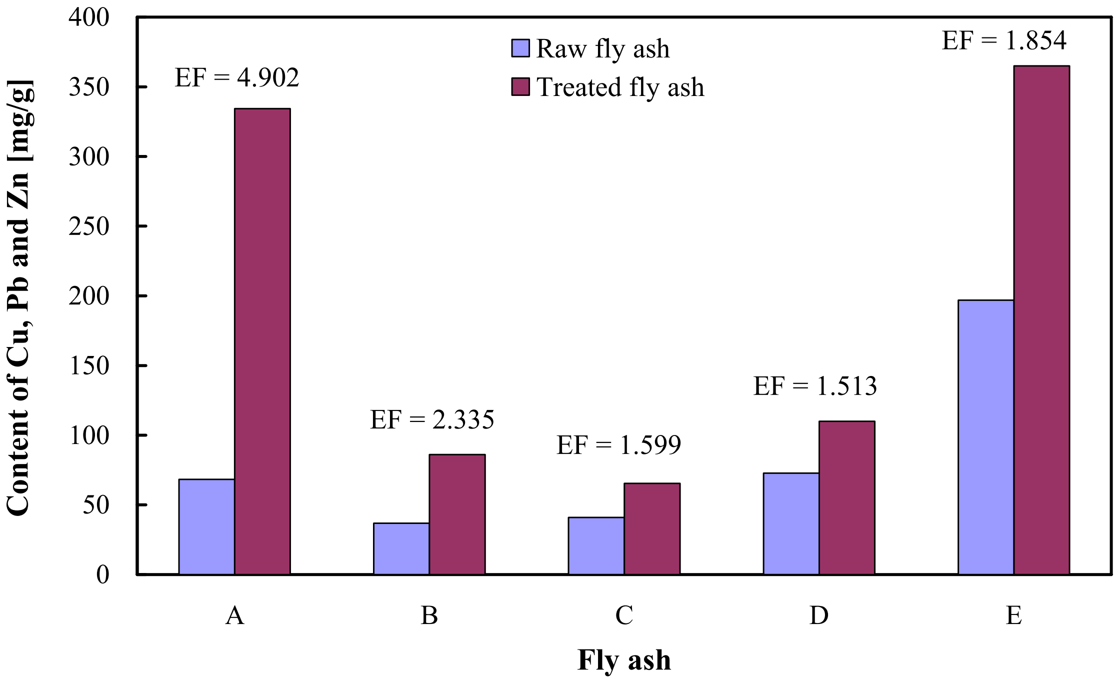


Fig. 6.5: Enrichment factor obtained for each fly ash

As a result of removal of soluble salts of NaCl, KCl and $CaCl_2$, the content of heavy metals in the filter cakes of treated fly ashes significantly increased and this increase was evaluated using an enrichment factor *EF* (Eq.(6.2)). **Figure 6.5** shows the enrichment factor determined for each fly ash and it can be seen that the values of *EF* varied from a value of 1.5 for Fly ash-D to a value of 4.9 for Fly ash-A.

In the next step, an attempt was made to find a relation between the enrichment factor and the composition of raw fly ashes in terms of the content of Na, K, Ca and chlorides. **Figure 6.6** shows the enrichment factor plotted against the sum of Na and K in raw fly ashes representing easily removable salts of NaCl and KCl, and against chloride contents. From this figure, it was concluded that the enrichment factor increased with an increase in the contents of Na and K as well as an increase in the content of Cl^-. In addition, the comparison of the enrichment factor *EF* with the content of Ca representing less soluble compounds such as $CaCO_3$, $Ca(OH)_2$, $CaSO_4$ showed that the enrichment factor decreased with an increase in the content of Ca.

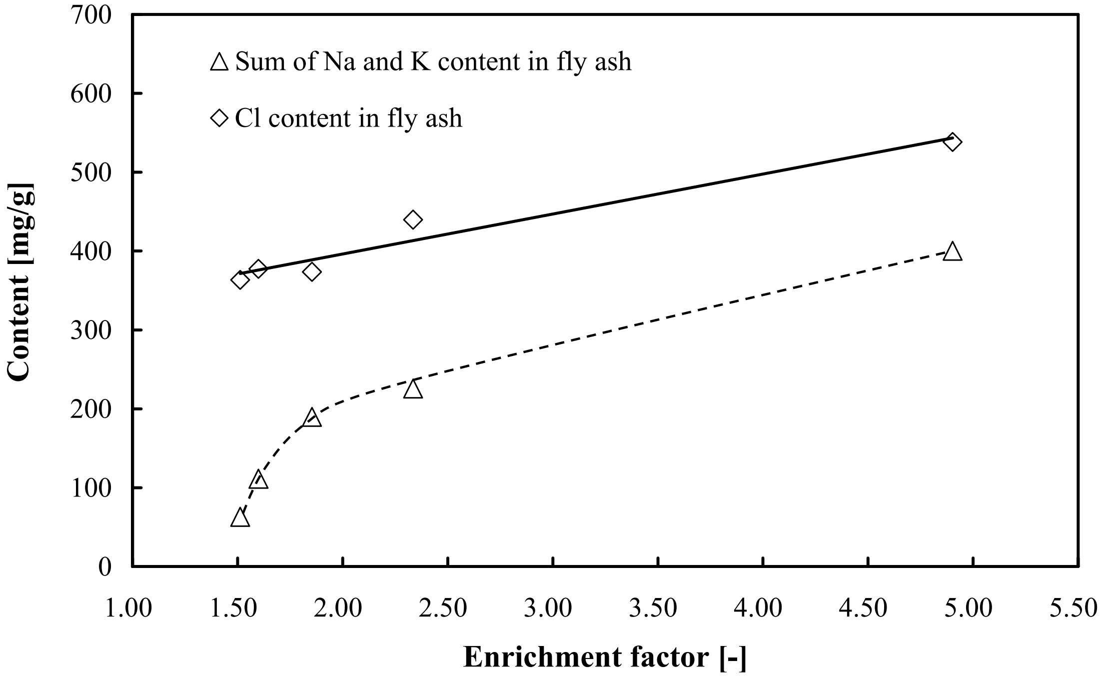


Fig. 6.6: Effect of Na, K and Cl content in raw fly ash on the enrichment factor of heavy metals

6.3.5 Analyses of treated fly ashes using XRD and SEM-EDS

Figure 6.7 shows the XRD patterns obtained for Fly ash-A to Fly ash-D after sulfidation treatment at the S^{2-} to Me^{2+} molar ratio of 1.00 for 0.5 hour. It can be seen that the characteristic peaks of NaCl and KCl were identified only in the case of Fly ash-A, but the intensities of these peaks were much lower than those of NaCl and KCl in raw Fly ash-A. Further, characteristic peaks of ZnS and PbS were found in the treated Fly ash-A, -B and -C confirming the formation of metal sulfides. The low intensities of characteristic peaks of metal sulfides shown in this figure probably resulted from a low content of metal sulfides as well as from a low crystallinity of the metal sulfides formed by the sulfidation treatment.

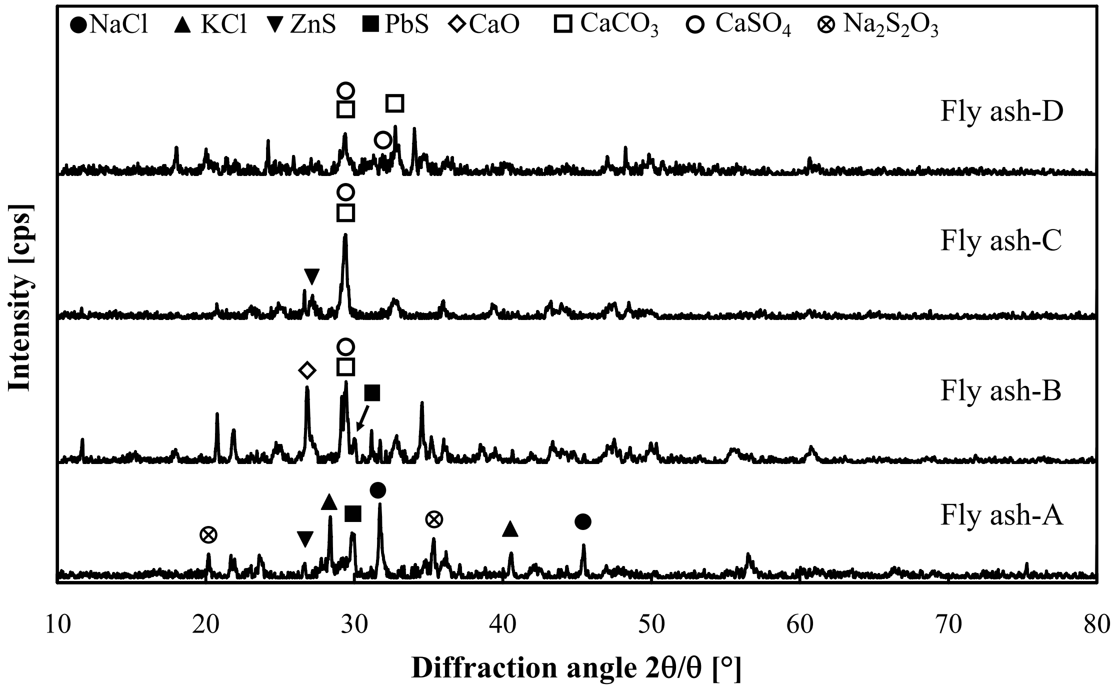


Fig. 6.7: Crystallographic composition of treated molten incineration fly ashes

In order to confirm the formation of metal sulfides, the treated Fly ash-A was subjected to SEM-EDS analysis. **Figure 6.8** shows a SEM image of a PbS particle as large as 10 μm identified in the Fly ash-A by means of electron dispersive spectroscopy (EDS). The EDS results for Zn, Pb, S and O are given in **Fig. 6.9**. Concerning the formation of ZnS, it can be seen from EDS maps of Zn, S and O (**Fig. 6.9**) that Zn and S atoms were located at nearly the same positions as O atoms and thus a clear identification of ZnS was prevented. This result suggested that the particles of ZnS formed by the sulfidation treatment were much smaller than the particles of PbS.

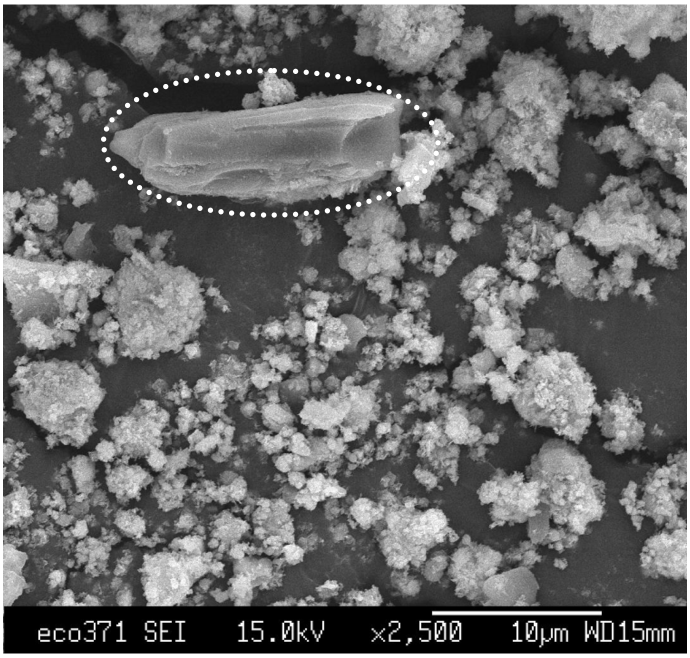


Fig. 6.8: SEM image of treated Fly ash-A

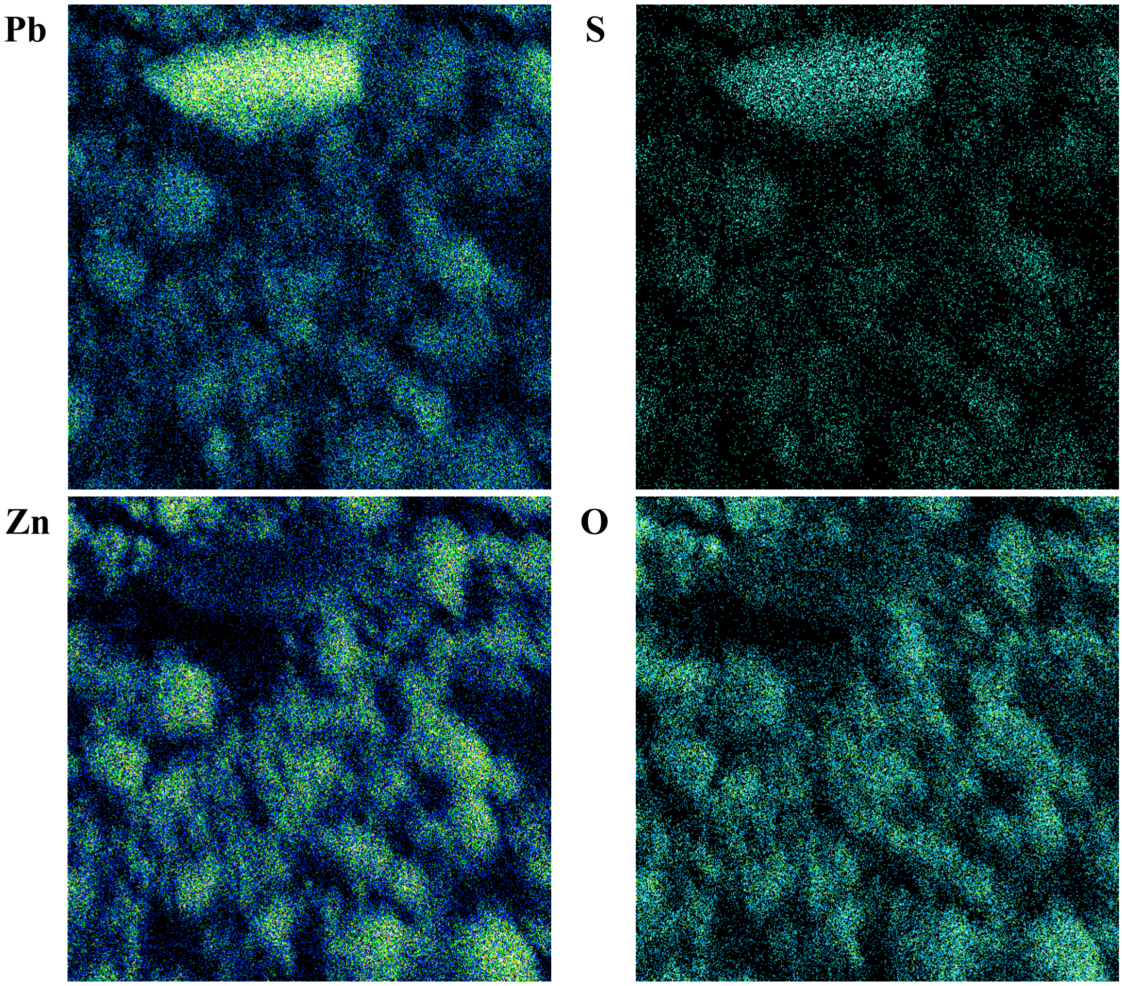


Fig. 6.9: EDS maps of Pb, Zn, S and O corresponding to SEM image (Fig. 6.8)

6.4 Conclusions

The sulfidation treatment of five molten incineration fly ashes with aqueous solution of Na_2S was carried out at a period of 10 minutes to 6 hours in order to convert heavy metals to metal sulfides, which could be thereafter separated by flotation. The main conclusions obtained in this study are drawn as follows:

- In the case of Fly ash-A to Fly ash-D, it was found that more than 79% of heavy metals of zinc, lead and copper was converted to metal sulfides within the contacting period of 0.5 hour owing to a fast conversion of metal chlorides to metal sulfides. On the contrary, the conversion of only 34% was achieved for Fly ash-E at the same contacting period, which was attributed to a high content of metal oxides, especially ZnO.

- When the S^{2-} to Me^{2+} molar ratio was reduced to 1.00 in order to minimize Na_2S consumption, the conversion varied from the lowest value of 0.758±0.001 for Fly ash-D to the highest value of 0.910±0.003 for Fly ash-C, after the sulfidation period of 0.5 hour.
- Further, the removal of soluble salts brought about a significant enrichment in the content of heavy metals by a factor varying from 1.5 for Fly ash-D to 4.9 for Fly ash-A. It was also found that the enrichment factor increased with an increase in the contents of Na and K as well as an increase in the content of Cl^-, but decreased with an increase in the content of Ca. Concerning the removable salts of NaCl and KCl, which may be a secondary problem, Katsuura et al. (1996) proposed that sodium-rich filtrates obtained after the acid extraction process of heavy metals could be subjected to purification and crystallization processes to obtain a raw material for sodium industry. Thus, it is considered that a similar procedure would be applicable to recover sodium and potassium from the filtrates remaining after sulfidation process.
- Finally, the formation of metal sulfides was confirmed by X-ray powder diffraction analysis and by scanning electron microscopy - energy dispersive spectrometric analysis.

6.5 Nomenclature

EF	enrichment factor [-]
$m_{\text{Me-treated FA}}$	total amount of Zn, Pb and Cu in the treated fly ash [mg/g]
$m_{\text{Me-raw FA}}$	total amount of Zn, Pb and Cu in raw fly ash [mg/g]
n_{Sa}	initial amount of sulfide [mol]
n_{Sb}	amount of sulfide ions consumed during blank experiment [mol]
n_{Sc}	amount of residual sulfide ions [mol]
n_{Me}	total amount of Zn, Pb and Cu involved in given molten incineration fly ash [mol]
X	conversion [-]

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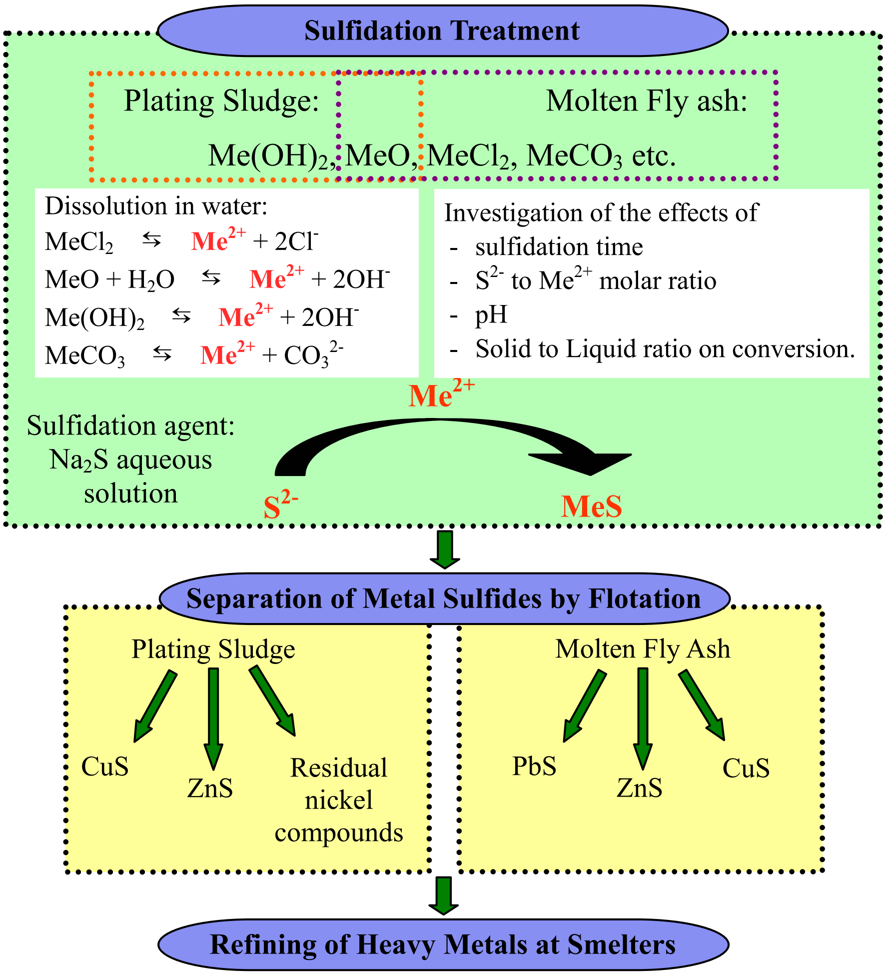
CHAPTER 7

Concluding remarks



The study on sulfidation treatment of plating sludges and molten incineration fly ashes was conducted in this dissertation work and it was found that the heavy metals present in these two types of industrial waste can be converted to metals sulfides. After the sulfidation treatment, heavy metals could be separated by flotation technique and subjected to the metal refining process at smelters.

7.1 General conclusions

The achievement of sustainable development requires, among others, an establishment of steady supply of important mineral resources including, coal, crude oil, natural gas as well as engineering metals. However, the primary mineral resources deposited in the Earth's crust are limited and inevitably susceptible to depletion. Therefore, when considering the energy demand, a continuous effort towards development of alternative energy sources such as solar, wind, geothermal energy to replace coal and oil as the most important energy sources is essential and indeed this effort has increased over the last several decades. Similarly, in the case of metal resources, a replacement of engineering metals with other materials such as plastics and establishment of highly efficient metal recycling system are needed to preserve mineral deposits for future generations.

Regarding the metal recycling system, it should be noted that metals have been recycled for very long time, but the efficiency of the recycling is relatively high only for metallic forms of heavy metals such as pure metals and their alloys, but the efficiency remains still low in terms of total metal consumption. The low recycling efficiency is attributed to heavy metals application in various products of industrial and daily use as well as to the generation of many kinds of wastes containing the valuable metals at quite low concentrations. As a consequence, valuable metals are disposed of to landfill sites rather than recovered to achieve complete cycling of metals. Given this, an improvement of collection system of these products/waste and establishment of an advanced recycling society is a challenging task.

In this dissertation work, an establishment of the complete cycling of heavy metals of copper, lead, nickel and zinc was targeted and to achieve this aim a recovery way of these heavy metals from two important types of waste, namely plating sludge and molten incineration fly ash from the incineration process of municipal waste or automobile shredder residues was proposed. In Japan, the amount of plating sludge generated annually amounts to 65,000 tons, while the amount of incineration residues (fly ash and bottom ash) from the incineration process of municipal waste is approximately 5.7 millions tons. As for the automobile shredder residues, an amount of about 9.09 millions tons of automobile shredder residues is reported to be generated every year and the major part of automobile shredder is incinerated, which leads to the production of a huge amount of incineration residues. As shown in the introduction, the plating sludges as well as molten incineration fly ashes contain heavy metals such as copper, lead, nickel and zinc at the concentrations comparable to those of heavy metals in natural ores, and hence, these wastes represent an important secondary source of heavy metals. As a recovery way, the sulfidation treatment was proposed and the sulfidation behaviour was thoroughly investigated using metal reagents, simulated and real plating sludges and various molten incineration fly ashes. The main findings obtained in the dissertation thesis are summarized as follows:

(1) In Chapter 2, it was presented that $Cu(OH)_2$ can be easily converted to copper sulfide, while the conversion of ZnO to ZnS was found to be much slower and strongly dependent on pH of the reacting system. The conversion of $Ni(OH)_2$ was found to be very low even after 7 days of contacting the solid sample of $Ni(OH)_2$ with aqueous solution of Na_2S.

The sulfidation treatment of various solutions containing heavy metals has been well reported in the literature, but the data on a direct sulfidation of solid metal reagents were scarce. Therefore, the investigation on sulfidation behaviour of reagents of $Cu(OH)_2$, ZnO and $Ni(OH)_2$ was carried out in this study as the first step in the effort to apply sulfidation treatment in the recovery process of heavy metals. The results showed that the sulfidation treatment can be easily used to convert solid reagent of $Cu(OH)_2$ to various copper sulfides within a short period of 1 hour and the conversion was found to be independent of solid to liquid ratio. In the case of ZnO, much longer time was required for conversion of ZnO to ZnS, and the conversion strongly depended on the solid to liquid ratio (on pH value of the reacting system). This result suggested a need for further investigation of the effect of pH on the conversion of ZnO to ZnS. In the case of $Ni(OH)_2$, only limited amount of $Ni(OH)_2$ was converted to nickel sulfides after 7 days of sulfidation period and thus, it was concluded that the sulfidation treatment is not suitable for the conversion of solid sample of $Ni(OH)_2$ to nickel sulfides. Finally, in spite of the low conversion of $Ni(OH)_2$, a treatment procedure was proposed to recover Cu, Zn and Ni from mixed plating sludges composed of these metals. At first, the sulfidation treatment is applied to convert copper and zinc to metal sulfides (further investigation is needed for zinc), and then these metals are separated by means of flotation. The flotation residue composed mainly of nickel compounds could be subsequently treated to recover nickel resource.

(2) In Chapter 3, the results obtained with $Cu(OH)_2$ were confirmed for simulated and real copper plating sludge.

Following the sulfidation of $Cu(OH)_2$, another step towards the recovery of heavy metals was taken in Chapter 3 and the sulfidation treatment was carried out for simulated and real copper plating sludge. It was confirmed that the conversion proceeded at a high reaction rate and the XRD analyses of sulfidation products obtained after 5 minutes of sulfidation treatment showed only peaks of copper sulfides for both sludges used. Interestingly, various copper sulfides were formed when S^{2-} to Cu^{2+} molar ratio was varied from 1.00 to 1.50 in the case of simulated copper plating sludge, but only CuS was formed in the case of real copper plating sludge. Such a result was explained using Eh-pH diagram of $Cu\text{-}S\text{-}H_2O$ system at 298K. Finally, the conversion was found to be independent of the particle size of initial sludge in the range of 0 to 125 μm used in this study, but the particle size of the initial sludge had a strong effect on particle size distribution of sulfidation products obtained.

(3) In Chapter 4, the results obtained with ZnO were confirmed for simulated zinc plating sludge and real plating sludge with high content of zinc. Moreover, the importance of pH on the conversion of zinc compounds to ZnS was confirmed suggesting that pH conditions should be carefully controlled in the real application of the sulfidation treatment of sludges with high content of zinc.

Similarly as in the case of copper (Chapter 3), the experiments were conducted for zinc simulated plating sludge and real plating sludge with high content of zinc to confirm the previously obtained results for ZnO. Special focus was put on the effect of solid to liquid ratio and effect of pH on the conversion of Zn compounds to ZnS. Similarly to the results obtained for ZnO, it was found that the conversion increased with an increase in pH value of the reacting system. However, the conversion of zinc compounds of the simulated plating sludge to ZnS proceeded in a higher rate than that of ZnO and also a higher conversion of about 80.9% was achieved. Regarding the sulfidation products, the XRD analysis of sulfidation products obtained after 48 hours at S:L ratio of 1:50 showed that only ZnS was present in the sulfidation product, which indicated that some unreacted zinc sludge remained enclosed in the agglomerates of ZnS formed. Finally, the results obtained for simulated sludge were confirmed using real sludge with high content of zinc.

(4) In Chapter 5, the applicability of the sulfidation treatment to molten incineration fly ashes was investigated and it was found that the heavy metals involved in molten incineration fly ashes can be converted to metal sulfides.

Following the successful sulfidation experiments of plating sludges, a study was conducted to verify the applicability of sulfidation treatment to molten incineration fly ashes. The direct sulfidation treatment with subsequent flotation of metal sulfides is assumed to be an adequate alternative to recently proposed recovery way for heavy metals from molten incineration fly ashes, which inheres in heavy metals extraction using an acidic medium and subsequent precipitation of metal ions as metal sulfides. In both cases, the metal sulfides are supposedly sent for further treatment at smelters. The experimental results summarized in Chapter 5 showed that the sulfidation treatment is indeed applicable to molten incineration fly ashes and the conversion of heavy metals to metal sulfides higher than 80% was achieved within 48 hours of sulfidation treatment. Finally, the results indicated that a significant enrichment of heavy metals could be achieved owing to the removal of soluble salts.

(5) In Chapter 6, the sulfidation treatment was conducted for five different molten incineration fly ashes and the conversion of about 80% was achieved for four fly ashes within 30 minutes of sulfidation period. Further, the sulfidation treatment brought about the enrichment of heavy metals in the treated fly ashes by a factor varying from 1.5 to 4.9 owing to the removal of soluble salts.

The encouraging results summarized in Chapter 5 gave rise to a more elaborated study on the sulfidation treatment of molten incineration fly ashes, during which five different molten incineration fly ashes denoted as Fly ash-A to Fly ash-E were used. Similarly to the results given in Chapter 5, the conversion in the case of Fly ash-A to Fly ash-D, was found to quickly increase to a value of about 80% within the contacting period of 0.5 hour, which was attributed to the fast conversion of metal chlorides to metal sulfides. By contrast, the conversion of only 34% was achieved for Fly ash-E at the same contacting period, which was attributed to a high content of metal oxides, especially ZnO. Based on these findings, it was concluded that the initial composition played a major role in the sulfidation of metal compounds involved in the molten incineration fly ashes and the conversion should be expected to decrease with an increase in the content of less soluble metal oxides such as ZnO. Finally, the removal of soluble salts brought about a significant enrichment in the content of heavy metals by a factor varying from 1.5 for Fly ash-D to 4.9 for Fly ash-A. It was also found that the enrichment factor increased with an increase in the contents of Na and K as well as an increase in the content of Cl^-, but decreased with an increase in the content of Ca.

7.2 Future research

The sulfidation treatment with subsequent flotation represents an important alternative to the acid extraction process followed by sulfide precipitation proposed in several studies to recover heavy metals from plating sludges and molten incineration fly ashes. The main advantage of the sulfidation process inheres in the fact that the treated plating sludges/molten incineration fly ashes can be directly subjected to heavy metals refining procedures currently used for mineral ores either alone or together with these mineral ores, and therefore, there is no need for huge initial investments as presumably in the case of acid extraction process.

The sulfidation process itself was thoroughly investigated in this dissertation thesis and thus a remarkable step in the sulfidation process with subsequent flotation was made, however there is still need for further investigation, especially in the area of flotation. The flotation process used in the processing of mineral ores is presently optimized to achieve the separation of the ore particles greater than 10 μm, but smaller particles of about 1 μm were formed in the sulfidation of zinc compounds. Thus, the study on optimization of flotation conditions for separation of smaller particles is required.

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