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Use of Monocalcium Phosphate Monohydrate for Chemical Immobilization of Heavy Metals Ions in Copper Smelting Slags

Monokalsiyum Fosfat Monohidrat Kullanımı ile Bakır İzabe Cürufundaki Ağır Metal İyonlarının Kimyasal İmmobilizasyonu

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Abstract

Monocalcium phosphate monohydrate (MCPM) with chemical formula of $Ca(H_2PO_4)_2.H_2O$ is a water-soluble and powerful agent for metal ion immobilization (removal) in soil and water. The use of MCPM can, therefore, be considered as an innovative and effective way to remove the leachable heavy metals from copper smelting slag. This study aims to (1) characterize copper smelting slag and perform the batch precipitation tests using MCPM, (2) analyze the treated copper smelting slag (residue) by x-ray diffraction (XRD) and (3) elucidate the mechanism of MCPM on leachable heavy metal removal from slag.

The experimental results demonstrated that MCPM effectively removes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn metal ions from copper smelting slag under different MCPM concentrations and reaction times. In addition, the XRD analysis reveals the formation of insoluble metal phosphates such as $Cd_3(PO_4)_2$, $Cu_2(PO_4)_2OH$, $Fe_3(PO_4)_2$, $Mn_3(PO_4)_2$, $Pb_3(PO_4)_2$ and $Zn_3(PO_4)_2$ in the residue of copper smelting slag.

Kewords: *Immobilization of heavy metals, Copper smelting slag, Characterization, Monocalcium phosphate monohydrate, Precipitation.*

Öz

Kimyasal formülü $Ca(H_2PO_4)_2.H_2O$ olan monokalsiyum fosfat monohidrat (MCPM), toprakta ve suda metal iyonlarını immobilize etmek için suda çözünebilen güçlü bir maddedir. Bu nedenle, MCPM kullanımı, bakır cürufundan çözünebilir ağır metallerin uzaklaştırılmasında yenilikçi ve etkili bir yol olarak düşünülebilir. Bu çalışmada; (1) bakır cürufunu karakterize etmek ve MCPM kullanarak bazı metallerin çökeltilmesini sağlamak, (2) metal uzaklaştırma (çökeltme) işleminden sonra elde edilen atığın x-ışını kırınımı (XRD) ile faz yapısını belirlemek, (3) cüruftan çözünebilir metal iyonların uzaklaştırılmasında MCPM mekanizmasının açıklanması amaçlanmıştır.

Deneysel sonuçlar, MCPM'nin farklı MCPM konsantrasyonları ve reaksiyon süreleri altında cüruf atığından Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr ve Zn metali iyonlarını etkin bir şekilde uzaklaştırdığını göstermiştir. Ayrıca, MCPM ile çöktürme işlemlerinden sonra elde edilen çökeltinin $Cd_3(PO_4)_2$, $Cu_2(PO_4)_2OH$, $Fe_3(PO4)_2$, $Mn_3(PO4)_2$, $Pb_3(PO_4)_2$ ve $Zn_3(PO4)_2$ gibi çözünmeyen metal fosfat yapılarını içerdiği XRD analizleri ile tespit edilmiştir.

Anahtar Kelimeler: *Ağır metal immobilizasyonu, Bakır cürufu, Karakterizasyon, Monokalsiyum fosfat monohidrat*, Çökeltme

1. Introduction

Metal mining or smelting operations and inappropriate discharge of industrial wastes have resulted in the contamination of terrestrial and aquatic environments with heavy metals. In addition, human exposure to heavy metals has been associated with several human diseases such as cardiovascular disease, cancers, memory deficits, chronic anemia, and kidney, nervous system, brain, skin, and bone damage [1-3]. In order to clean up waste or wastewater containing toxic metal (heavy metal) ions, efforts have been taken by using remediation technologies. According to Quina et al. [4], the most common remediation methods used to remove heavy metals from an aqueous solutions and contaminated mining wastes were chemical precipitation, ion exchange, membrane filtration, solvent extraction, flotation, adsorption, bioremediation, phytoremediation. Due to the limitations and operating cost of these methods, numerous studies were performed on heavy metals stabilization using phosphate based-materials (phosphate rock (PR), diammonium phosphate (DA), monocalcium phosphate monohydrate (MCPM), hydroxyapatite (HA), etc.) [5-18]. In this study, MCPM called also triple superphosphate was selected amongst various phosphate sources and fertilizers to act as a precipitating agent for the removal of heavy metals from copper smelting slag. Researchers in soil science have shown the ability of MCPM to dissolve and stabilize metals [19-24]. In our previous study on the removal of lead from aqueous solutions by TSP, the formation of lead phosphate was determined by stability area diagrams and was confirmed by precipitation test and x-ray diffraction analysis of Pb precipitate [25]. Despite, the ability of MCPM in metal fixation, there are few experimental studies on the treatment of mining or smelting waste containing toxic metal ions together (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn).

The purposes of this study were to (1) perform the batch precipitation tests to stabilize copper smelting slag with MCPM, (2) analyze the treated copper smelting slag (residue) by x-ray diffraction (XRD) and (3) elucidate the mechanism of MCPM on hazardous metal removal.

2. Materials and Methods

Monocalcium phosphate monohydrate (MCPM) used in this study is a fertilizer and was received from a Gübretaş company in Turkey. The particle size of MCPM was below 0.5 cm when it arrived and it was ground to below 100 µm to use in the experiments. Its moisture content was 2% as received.

2.1. Characterization method

The characterization includes the physicochemical properties of copper smelting slag by analyzing particle size distribution, chemical composition and x-ray diffraction (XRD) analysis. For this purpose, the collected slag sample from copper smelter in Turkey was ground by agate mill disc, homogenized and split using rotary sample division to ensure its representativeness. The particle size of the ground sample was determined by the Horiba LA-950 laser particle size distribution analyzer.

The chemical composition test was carried out by digesting 0.2g of copper smelting slag with the addition of 10 ml HNO_3, 5ml HF and 5ml distilled water using a microwave (Model: Mars 6240/50) digestion system. Afterward, the collected leachate solution was transferred into a volumetric flask and adjusted to 250 ml volume using distilled water. Thus, concentrations of heavy metals were determined by inductively coupled plasma (Model: Varian 710-ES ICP-OES).

Initial pH is determined by transferring 5 g of copper smelting into 100 ml distilled water.

The mineralogical composition of the copper smelting slag sample was identified by Philips X'Pert Pro diffractometer (Cu Kα radiation: 1.5418 Å, 45 KV, 40 mÅ).

2.2. Precipitation experiment

The precipitation tests were conducted at room temperature in accordance with the previous experimental procedures on chemical stabilization using phosphate amendment [26]. First, a mixture of 25 copper smelting slag containing metals ions (L/S=20) and different amounts (12.6, 25.2 and 63.0g) of MCPM (equivalent to 0.1, 0.2 and 0.5 M or mol/L) were dissolved in glass beakers containing 500ml distilled water and agitated with magnetic stirring bar for 30 minutes. The pH of the solution was adjusted and maintained at 5 with a small addition of nitric acid or NaOH during testing. After 30 minutes of the solubility test, samples of 5 ml were taken at different time intervals of 0, 5, 10, 15, 30, 60, 120 and 180 minutes and filtered immediately using 0.2 µm syringe filters. The concentration of metals in each sample was determined by inductively coupled plasma (model: Varian 710-ES ICP-OES) with operating conditions as follows: RF Power: 1300 W, plasma flow rate: 15 L/min., Nebulizer flow rate: 0.7 L/min. and Auxiliary flow rate: 0.2 L/min. Calibration of the device was performed before sample injection by using 2.0 mg/L of Cd, 5 mg/L of Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn standard solutions and repeated 10 times. For the accuracy of collecting data (Table 1), quality assurance and quality control (QA/QC) are performed following the experimental design described by Taşgetiren [27].

2.3. Mineralogical (XRD) analysis of raw MCPM and copper smelting slag residue samples

The obtained residue (copper smelting slag treated by MCPM) after the precipitation test, was filtrated through a filter paper (Reeve angel-grade: 307; size:125mm), then the solid contents were oven-dried at 105°C for 1 hour, cooled in a desiccator and ground to a size below 100µm using a motor grinder (MG100/MG200). The dry residue and raw MCPM were analyzed by Philips X'Pert Pro diffractometer (Cu Kα radiation: 1.5418 Å, 45 KV, 40 mÅ).

3. Results and Discussions

3.1. Physicochemical properties of copper smelting slag

As plotted in Figure 1, the particle size analysis indicates 80% of ground copper smelting slag particles are under 82.4µm and 30% of particles are below 17.7µm. The mean of the particle distribution is 52.40µm.

The chemical composition of copper smelting slag is shown in Table 2. The results demonstrated that the copper slag sample contains Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn heavy metals. Further, high chemical oxides contents of Fe_2O_3 (56.57%) and SiO_2(36.14%) were observed in the analyzed copper smelting slag sample. The results of chemical oxides found in this research are similar to those published previously [28]. The measured pH of copper smelting slag sample by pH meter (Orion 4 Star) was 8.6 in water.

Figure 2 shows the x-ray diffraction (XRD) pattern of copper smelting slag. As seen in Figure 2, fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) are the main mineral compounds in the copper smelting slag. In some peaks, quartz (SiO_2) is also identified. Similarly, İbrahim [29-31] reported that fayalite and magnetite are abundant in the copper slag, whereas the presence of quartz is low.

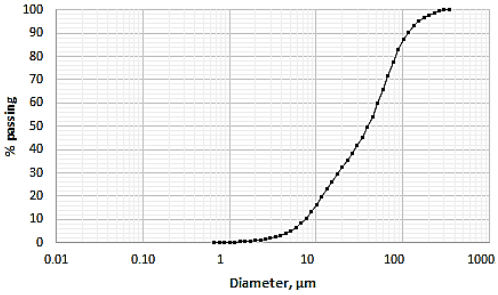

Figure 1. Particle size distribution of copper smelting sample.

Table 1 Limit of detection (LOD) and Limit of quantifications

Standard Metals Concentrations (mg/L)	Measured Concentrations (mg/L)										Means	SD(±)	LOD	LOQ
Cd	2.04	2.06	2.03	1.98	2.04	2.04	2.01	2.02	2.02	1.97	2.0202	0.0279	0.0836	0.2786
Co	5.02	5.05	5.05	4.95	5.08	5.07	4.97	5.04	4.99	4.98	5.0210	0.0451	0.1354	0.4514
Cr	4.97	5.06	4.98	4.96	5.01	5.04	4.98	5.03	4.96	4.99	4.9973	0.0353	0.1060	0.3532
Cu	5.05	5.01	5.07	4.96	5.08	5.06	5.02	5.07	5.01	4.98	5.0303	0.0397	0.1191	0.3971
Fe	5.07	5.03	5.04	4.98	5.06	5.07	4.97	5.03	4.99	4.97	5.0218	0.0390	0.1171	0.3904
Mn	5.06	5.06	4.98	4.98	5.04	5.03	5.02	5.03	5.02	5.03	5.0244	0.0285	0.0855	0.2850
Ni	5.00	5.08	5.02	4.97	5.04	5.00	4.94	5.02	4.97	4.96	4.9986	0.0417	0.1252	0.4173
Pb	4.98	5.03	4.99	4.99	5.04	5.01	4.98	5.05	4.95	4.97	4.9982	0.0321	0.0964	0.3212
Sr	4.96	4.95	5.02	4.99	4.97	5.09	5.03	4.97	5.04	5.08	5.0084	0.0515	0.1546	0.5154
Zn	5.05	5.01	5.02	4.98	5.02	5.03	5.02	5.04	5.01	5.03	5.0208	0.0192	0.0576	0.1919

Table 2. Chemical composition of tested copper slag

Major elements (%)		Heavy metals (mg/Kg)	
SiO_2	36.14	Cd	20
Al_2O_3	2.97	Co	1040
Fe_2O_3	56.57	Cr	320
CaO	1.30	Cu	5460
MgO	0.67	Fe	39600
Na_2O	0.46	Mn	240
K_2O	0.72	Ni	30
MnO	0.03	Pb	2910
TiO_2	0.13	Sr	110
SO_3	1.28	Zn	31900

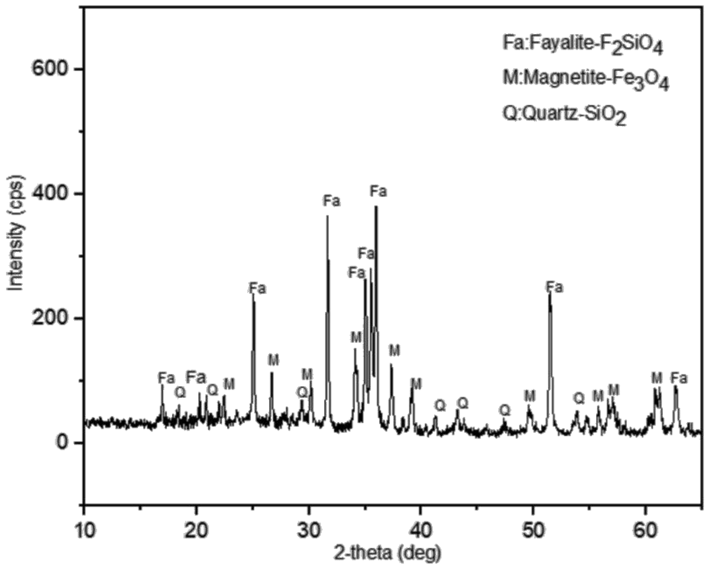

Figure 2. XRD pattern of copper smelting slag sample

3.2. Immobilization of heavy metals by MCPM

The use of MCPM to treat copper smelting slag under different conditions (liquid/solid ratio: 20, pH:5, reaction times and different MCPM concentrations) shows that MCPM removes heavy metals efficiently. The effect of reactions times and MCPM concentrations on the removal (immobilization) efficiency of heavy metals by MCPM was discussed below.

3.2.1. Effect of reaction times

The reaction time effect was conducted between 5 to 180 minutes using 0.1 M of MCPM. As shown in Figure 3, the reaction time increases the removal efficiency of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn metals. Similar findings were reported that the reaction time plays an important role in the immobilization of heavy metals by phosphate amendment [32]. The removal efficiency of heavy metals by MCPM ranged from 41.1% to 78.8% for Cd, 24.8% to 54.1% for Co, 24.6% to 52.4% for Cr, 12.4% to 42.2% for Cu, 32.1% to 77.5% for Fe, 30.0% to 53.3% for Mn, 19.6% to 52.7% for Ni, 56.7% to 98.9% for Pb, 37.8% to 72.7% for Sr and 18.6% to 50.4% for Zn at 5 and 180 minutes of reaction times respectively. However, except for Pb, Cd, Fe and Sr, low removal efficiency was observed for other metals at 180 minutes of precipitation times. It was also found that MCPM was able to precipitate up to 97% of Pb at only 30 minutes due to the high affinity of MCPM to bind with lead.

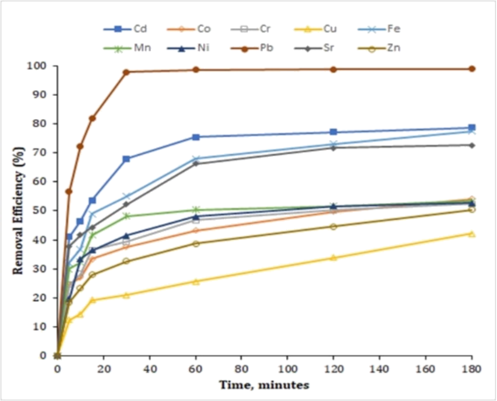

Figure 3. Effect of reaction times on immobilization of heavy metals from 25g copper smelting slag by 0.1M of MCPM.

3.2.2. Effect of MCPM concentrations

The effect of MCPM concentrations of heavy metals from copper smelting was investigated at 0.1, 02 and 0.5 M of MCPM. Figure 4 demonstrates that the excess addition of MCPM concentration leads to a high rate of heavy metals removal. The removal efficiency for all metals increased with increasing MCPM concentrations. At 180 minutes of precipitation test, it was found that 0.1 M of MCPM remove 78.8% of Cd, 54.1% of Co, 52.4% of Cr, 42.2% of Cu, 77.5% of Fe, 53.3% of Mn, 52.7% of Ni, 98.9% of Pb, 72.7% of Sr and 50.4% of Zn concentrations, while 93.2% of Cd, 79.3% of Co, 71.6% of Cr, 61.2% of Cu, 91.1% of Fe, 70.4% of Mn, 68.4% of Ni, 99.0% of Pb, 84.5% of Sr and 67.9% of Zn concentrations were removed from copper smelting slag by 0.2 M of MCPM. On the other hand, the high removal efficiency was achieved by 0.5 M of MCPM in which all metals concentrations were reduced by more than 90% except for Cu (83.7%) and Zn (86.6%). Feng et al [33] and Weber et al. [34] also stated that the use of excess phosphate-based materials including monocalcium phosphate monohydrate (MCPM), diammonium phosphate (DAP), hydroxyapatite (HA) is required to immobilize toxic elements such as Pb, Cd, Fe from the soil, water, and sludge.

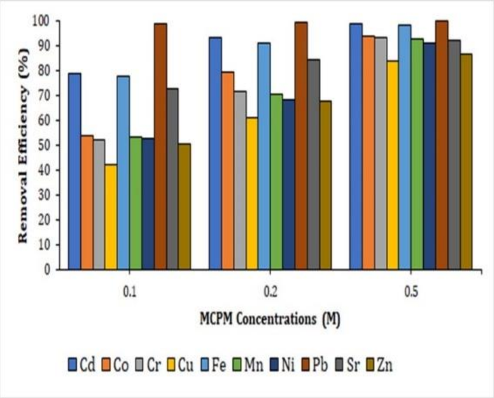

Figure 4. Effect of MCPM concentrations (0.1, 0.2 and 0.5 M MCPM) on immobilization of heavy metals from 25g of copper smelting slag at 180 minutes of precipitation process.

3.3. Mechanism of MCPM on heavy metal immobilization

The mineralogical composition of copper smelting slag residue was identified by x-ray diffraction (XRD). As illustrated in Figure 5, the main mineral compounds were fluorapatite [$Ca_5(PO_4)_3F$], Fayalite (Fe_2SiO_4), magnetite (Fe_3O_4) and quartz (SiO_2). The presence of fluorapatite is originated from the MCPM sample (Figure 6). Further, the formation of new compounds such as cadmium phosphate [$Cd_3(PO4)_2$], libethenite [$Cu_2(PO_4)_2OH$], iron phosphate [$Fe_3(PO_4)_2$], manganese phosphate [$Mn_3(PO4)_2$], lead phosphate [$Pb_3(PO_4)_2$] and zinc phosphate [$Zn_3(PO_4)_2$] were also observed in some peaks. Those metal phosphate compounds are sparingly soluble (insoluble) and their formation is elucidated by the MCPM mechanism on heavy metals. In other words, the mechanism of MCPM involves its dissolution (Equation (1)) and metal precipitation reactions (Equations (2), (3), (4), (5), (6) and (7)):

$$\text{MCPM dissolution: } Ca(H_2PO_4)_2.H_2O \rightarrow Ca^{2+} + 2H_2PO_4^- + H_2O \tag{1}$$

$$\text{Precipitation: } 3Cd^{2+} + 2H_2PO_4^- \rightarrow Cd_3(PO_4)_2 + 4H^+ \tag{2}$$

$$2Cu^{2+} + H_2PO_4^- + H_2O \rightarrow Cu_2(PO_4)OH + 3H^+ \tag{3}$$

$$3Fe^{2+} + 2H_2PO_4^- \rightarrow Fe_3(PO_4)_2 + 4H^+ \tag{4}$$

$$3Mn^{2+} + 2H_2PO_4^- \rightarrow Mn_3(PO_4)_2 + 4H^+ \tag{5}$$

$$3Pb^{2+} + 2H_2PO_4^- \rightarrow Pb_3(PO_4)_2 + 4H^+ \tag{6}$$

$$3Zn^{2+} + 2H_2PO_4^- \rightarrow Zn_3(PO_4)_2 + 4H^+ \tag{7}$$

Meanwhile, the XRD pattern of copper slag residue failed to show the formation of cobalt, chromium, nickel and strontium phosphates. In this case, the prior experimental studies indicated that multimetal phosphates can form with unknown or broadening peaks, making it difficult to identify the peak position [35].

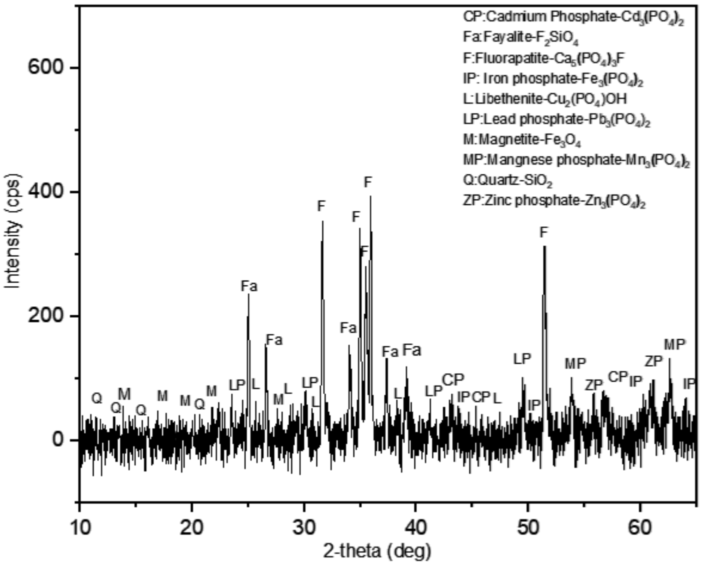

Figure 5. XRD pattern of copper smelting slag residue (Copper smelting slag treated by MCPM)

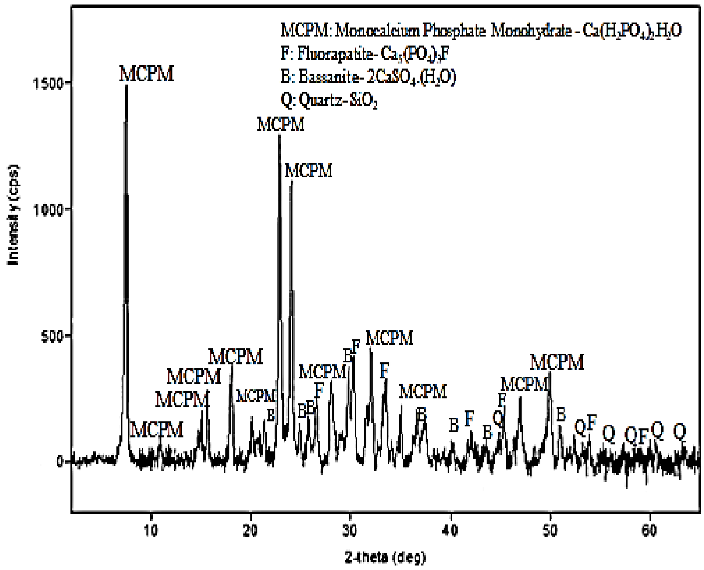

Figure 6. XRD pattern of MCPM as received

4. Conclusions

Immobilization of the heavy metals from copper smelting slag using monocalcium phosphate monohydrate (MCPM) was investigated in this study. The experimental results indicate that the reaction times and concentrations of MCPM parameters affect the removal efficiency of heavy metals during the precipitation process. Increasing reaction time and concentrations of MCPM promote a high removal of heavy metals and the percentages of removal are in order Pb (100%)> Cd (98.8%)> Fe (97.9%)> Co (93.7%)> Cr (93.3%)> Mn (92.7%)> Sr (91.8%)> Ni (90.7%)> Zn (86.6%)> Cu (83.7%) at pH 5. However, the excess addition of MCPM is required in order to achieve an effective immobilization of heavy metals. The XRD analysis reveals the formation of insoluble metal phosphates such as $Cd_3(PO4)_2$, $Cu_2(PO_4)_2OH$, $Fe_3(PO_4)_2$, $Mn_3(PO4)_2$, $Pb_3(PO_4)_2$ and $Zn_3(PO_4)_2$

in the residue of copper smelting slag. Indeed, MCPM is not only an effective precipitant agent to immobilize heavy metals, but it can also solve the problem of continuous monitoring of pH changes that lead to metal dissolution in aqueous environments.

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