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Convergence Process for the Removal of Heavy Metals in the Abandoned Mine

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휴폐광산의 중금속제어를 위한 융합공정 개발

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Abstract The convergence process utilized both leaching and ion exchange techniques has been investigated for the heavy metals removal in the abandoned mine of Chungyang Province, Korea. The contaminated soil samples by heavy metals from Samkwang mine were analysed by statistical analyses. The highly contaminated soils was initially separated by the flotation process. The selectivity indices were increased with increasing flotation reagents. The selectivity of separation was then improved by the use of both leaching and ion exchange processes in order to extract the heavy metals. The results of this study showed that the higher the sulfuric acid concentration, the leaching rate of heavy metals was increased. The lecheate then was removed by the ion exchange method. The anticipating results might imply that convergence process utilized both leaching and ion exchange techniques would somehow apply for the removal of heavy metals in the abandoned mine.

• Key Words : Convergence Process, Heavy Metals, Flotation, Leaching, Ion exchange

요 약 청양지역 폐광산의 오염원인인 중금속의 제거를 침출과 이온교환법을 활용한 융합공정을 통해 실험하였으며 중금속에 오염된 토양시료는 통계처리를 하여 분석하였다. 오염토양은 일차로 부선처리법으로 분리하였으며, 사용시약이 증가할수록 선별지수는 증가하였다. 중금속을 제거하기 위한 침출과 이온분리법에 의해 선별도는 더 향상이 되었다. 침출속도는 황산용액이 증가할수록 증가되었으며, 침출용액은 이온교환법에 의해 상당부분 제거가 되었다. 침출과 이온교환법이 결합된 연속융합공정을 개발하여 중금속 제거 실험을 하였으며, 향후 개선을 통해 중금속의 제거효과가 향상될 것이며, 이를 통해 폐광산의 오염토양에 적용 가능함을 알 수 있었다.

• Key Words : 융합공정, 중금속, 부선, 침출, 이온교환

1. Introduction

Many waste mine soils with large amount contain toxic heavy metals, which have to be removed prior to leach and to flow surface waters. Heavy metals in the soil of the abandoned mines are usually toxic and dangerous. Abandoning deserted mine areas is a common problem encountered at many hazardous

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waste sites with large amounts of heavy metals. Abandoned mines without proper treatment for a long time is problematic for the accumulation of mine wastes and tailings contaminate neighboring regions like river basins and residential districts. The accumulation in living tissues through the food chain poses a serious health hazard[1]. The gradual strict environmental regulations require for innovative treatment technologies in order to remove heavy metals.

The main minerals of the abandoned mine sites are composed of sulfide minerals. The problem is encountered by the weathering of waste materials which activates the oxidation reaction. The oxidized sulfide minerals cause the pH of the soil to decrease; the sulfide minerals containing heavy metals can be leached out of the soil easily depending on the pH and the concentration[2,3]. The mine and processing plants are often situated in water flow areas through mountain slopes and so environmental action plans are required to limit acid drainage and prevent pollution.

Mine drainage is highly acidic below the pH of 4 as the components and contents of the heavy metals are extremely high, causing contamination of the surrounding environment. Remediation of contaminated soil can be performed using in-situ and/or ex-situ techniques. Remediation techniques can be biological, physical or chemical. Biodegradation uses bacteria or fungi to remove contaminants in soil[1,4]. Typical methods employed for removal of heavy metals from the abandoned mines are soil washing, classification, flocculation and flotation techniques. Flotation is a separation technique based on the capture of particles by bubbles and their collection in the froth layer[4].

The main minerals in Samgwang mine are composed of pyrite(FeS2), galena(PbS), arsenopyrite (FeAsS), chalcopyrite(CuFeS2), and etc. Substituted minerals include quartz and sericite. The chemical analyses data and statistical analyses, As, Pb, Cd, Zn, Ni, and Cu are widely distributed not only in the mine regions but also in forests and farmlands[5]. Arsenic from arsenopyrite is found in the following substances: inorganic arsenic compounds like semi metallic element(0), arsenite(Ⅲ), andarsenate(Ⅴ), and organic arsenic compounds like MMA (mono methyl arsenic acid) and DMA (dimethyl arsenic acid)[3,6]. Ininorganic arsenic compounds, As(Ⅲ) is more toxic than As(Ⅴ). In the soil samples of current investigation, arsenic exists more commonly as arsenate than arsenite[5].

The purpose of this study is to develop the optimum convergence process to effectively remove the heavy metals that causes the greatest risk to human health. The flotation separation, leaching and ion exchange tests were conducted with soil samples in order to give information to find variables and promote remediation of contaminated soil.

2. Materials and Methods

2.1 Materials

The soil samples were collected in the Samkwang mine which have a longitude of 360° 31‘ 04” and a latitude of 126° 52‘ 50”. As the heavy metals within the soil of the mine exist mostly within 4,000 meters, the samples were collected in the Northern, Southern, Eastern, and Western directions within 50 meter intervals. The soil samples were screened out by wet analysis technique and dried for measuring heavy metal contents by ICP(Flame Module S). Baker analytical reagent grade sulfuric acid was used. All reagents were analytical reagent grade and purchased from Fisher Co. The pH value was adjusted by the addition of sulfuric acid or sodium hydroxide solutions when needed. The collector emulsion was prepared by various concentrations of SDS (sodium dodecyl sulfate). The correlation analysis was performed between the heavy metals in the soil.

〈Table 1〉 Chemical Composition of Soil Sample Analysed ICP (ppm)

As	Zn	Cd	Pb	Ni	Cu	Cr	Hg
152	95.91	3.73	26.78	4.46	4.89	N.D	N.D

2.2 Methods

The flotation treatment was conducted with soil samples in the range of -420μm to +43μm. The floated samples were used for leaching and ion exchange tests. The batch flotation tests are conducted with a 20 g (dry basis) sample in a homemade laboratory flotation cell to 25% solids. The sample was then agitated for 1 minute at 900 rpm with a predetermined amount of sulfuric collector and floated for 1 minute.

The leaching experiments were made with a 3-liter scale leaching cell. The percent leaching efficiency was expressed as the percentage of the content quantity of the initial sample from the leacheate. The heavy metals in leacheate were then removed by ion exchange processes. The ion exchange experiment was conducted with a 5 cm diameter and a 20cm height acryl tube column. The column was filled with synthetic resins in a study for adsorption rate as a function of bed volume.

3. Results and Discussion

Waste mine wastes and their mine drainages contain high amounts of heavy metals (e.g. Cu, Pb, Cd, and As). Contaminated crops after leacheate from mine can accumulate within the organs and thus cause terminal diseases to biosphere. In order to reduce the risk of contamination with heavy metals from mine wastes, the processes must be treated effectively. The statistical methods was performed to evaluate pH and the contamination levels of the following elements within the polluted soil surroundings: As including other seven heavy metals, Cd, Cu, Hg, Pb, Ni, Cr6+, and Zn. <Table 2> represents the summary of statistics for element's mean concentrations of heavy metals in soil. The mean dispersion, standard deviation (SD), and the coefficient of variation(CV) were calculated[6], and it was found that out of the heavy metals, Zn was the most detected element. The coefficients of variation can be ranked as follows Pb > Ni > Cu > Cd > As. The contents of Hg and Cr6+are minial compared other six heavy metals.

<Table 3> represents the correlation matrix of the components of heavy metals that influences the contaminated soil. '*' in the correlation matrix indicates a significant correlation at the 5% significant level, whereas '**' indicates at the 1% significant level. In this <Table 3>, As, Cd, and Cu have the highest correlation, on the other hand, the correlation of Pb is rather low. Therefore, the heavy metal ions of soil in Samkwang mine may exist scattered in the wide range and not homogeneous[7].

Although a hydrometallurgical process is still favored for treating the contaminated soils, flotation can be a potential alternative if a suitable flotation agent is available. Flotation which is one of the major important minerals beneficiation techniques has found extensive use in wastewater technology due to its convenience[8]. SDS are the most and extensively used collectors for silicates. Therefore, the use of SDS as a collector to remove silicates from the heavy metals is expected to be allow selectivity.

〈Table 2〉 Summary of Statistics for Element's Mean Concentrations of Heavy Metals in Soil (mg/Kg)

Variable	n	Mean	SD	CV	Min.	Max.
pH	23	6.289	0.706	11.236	5.1933	7.8242
As	23	2.7960	7.4354	265.928	0.02250	26.267
Cd	23	2.7704	7.2336	261.100	0.08367	31.307
Cu	23	1.321	0.0665	88.9133	3.75283	41.950
Ni	23	23.201	10.198	43.9547	9.16000	46.917
Pb	23	122.31	374.22	305.947	4.19667	1696.0
Zn	23	313.89	922.64	293.930	44.19667	4487.0
Hg	23	0.0095	0.0099	103.651	0	0.0402
Cr+6	23	0.0022	0.0107	479.583	0	0.0516

〈Table 3〉 Correlation Matrix for Soil Contamination Data.

	pH	As	Cd	Cu	Ni	Pb
pH	1.000					
As	0.628**	1.000				
Cd	0.599**	0.171	1.00			
Cu	0.370	-0.01	0.76	1.00		
Ni	0.239	0.404	0.35	0.12	1.000	
Pb	-0.038	-0.10	0.04	0.26	-0.02	1.00

Leaching is the process of dissolving the metals from the contaminated soils or minerals and extracting the metals of interest into the solution[10]. The leach liquor then is further purified before the metal values are recovered. Most soils containing heavy metals are leacheable in sulfuric acid.

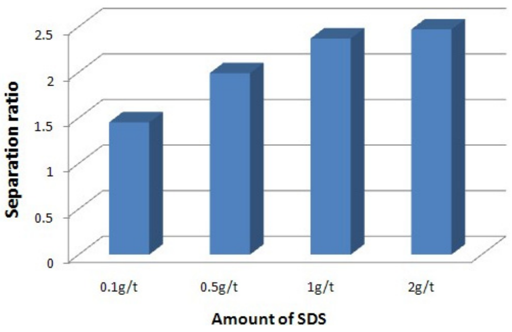
The almost half of the contaminated soil samples was considered -35㎛ fines. This fine particles that were analyzed with a pcynometer were composed of mainly sand, silt, and clay etc. [Fig. 1] shows the flotation results with a SDS collector at natural pH.

The anionic collector, SDS, was proven to be effective collector for the silicate samples[8]. To investigate how SDS respond to the flotation of soil samples, a series of batch flotation tests were carried out. The flotation results are shown in [Fig. 1] in terms of separation ratio. The separation ratio[9] is expressed as the geometric average of the ratio of the recoveries of silicates Q to heavy metal, M, in the froth products, F, and of M to Q in the cell products, C:

$$S.I = \sqrt{\frac{Q_F M_C}{M_F Q_C}} \qquad (1)$$

The separation ratio is unified when there is no separation, and it is infinite when the separation is perfect. The concentrations of As, Pb, Cd were determined from froth and cell products, respectively. The separation ratios of As, Pb, Cd are shown in [Fig. 1]. The flotation selectivity was obtained by using SDS. However, when the concentration of SDS was increased to 5 g/t, the separation ratio was minimal. The effective separation was obtained when 0.5 g/t SDS was used.

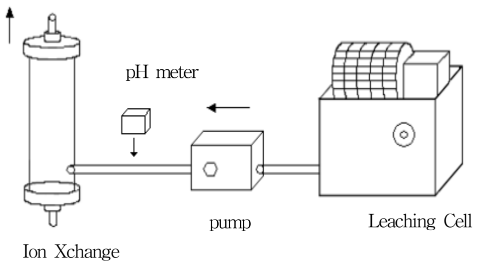
The oxidized soil samples from the contaminated soils have a large proportion of carbonates or clays. Flotation may not be economically favorable because the obtaining a good separation is necessary for large consumption of flotation reagents and complex process. Much research is needed in order to solve this problem of flotation of the heavy metal contaminated soils from abandoned mine and to arrive at the efficient flotation system.



[Fig. 1] Separation Ratios of Heavy metals for the Effect of the Amount of SDS.

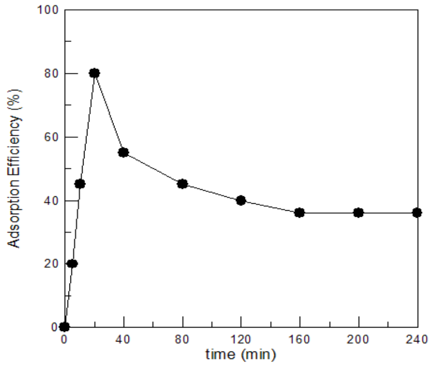
The convergence processe utilizing leaching and ion exchange may be much potential alternative for processing of the contaminated soil samples by heavy metals. Also it would be very economical to process the fine contaminated soils.

[Fig. 2] shows the schematic diagram of the continuous convergence process of leaching and ion exchange cell. More details of each cells are given in Methods section.



[Fig. 2] Convergence Process of Leaching and Ion exchange Cell.

The continuous leaching and ion exchange system were performed. The ion exchange tests were conducted by using anionic ion exchange resin[11]. [Fig. 3] shows the adsorption efficiency of heavy metals using the convergence process. The heavy metal ions were able to adsorb well with increasing reaction time. When the reaction time is 20 minutes, 80% of heavy metal ions was adsorbed. The heavy metals were decreased gradually with increasing time. This phenomena might be contributed that the surface pore of ion exchange resin was blocked by fine particles during the process[12]. The desliming should be necessary for the successful operation.



[Fig. 3] Adsorption Efficiency of Heavy metals by Convergence Process as a function of Reaction Time.

4. Conclusions

The convergence process utilized both leaching and ion exchange techniques has been investigated for the heavy metals removal in the abandoned mine. The soil surrounding abandoned mine contains a huge amount of heavy metals and therefore are not treated well yet. The following conclusions may be drawn:

1. The statistical methods were used for the comparison. Statistical analyses showed that the correlation between As, Cd, and Cu have the highest correlation, on the other hand, the correlation of Pb is rather low.
2. On the flotation results, the use of SDS improved the selectivity of separation. The separation ratios was almost 2 at the amount of 0.5 g/t SDS.
3. Leaching tests were conducted with sulfuric acid. The higher the sulfuric acid concentration, the leaching rate heavy metals was increased. The lecheate then was removed by the ion exchange method.
4. The convergence process was used. The anionic ion exchange resin adsorbed heavy metals well with increasing reaction time. The adsorption efficiency was almost 80%. As time passed, however, the effectiveness of adsorption rate was decreased tp 40%. It is noteworthy that this phenomena might be contributed that the surface pore of ion exchange resin was blocked by fine particles during the process

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