pISSN 1229-3008 eISSN 2287-6251
Progress in Superconductivity and Cryogenics
Vol.21, No.2, (2019), pp.31~35 https://doi.org/10.9714/psac.2019.21.2.031

Evaluation of contamination for the Andong-dam sediment and a magnetic separation for reducing the contamination level

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(Received 21 March 2019; revised or reviewed 9 May 2019; accepted 10 May 2019)

Abstract

Andong-dam was built up in 1967 and it is one of the biggest dams in Korea. Previous studies showed that the sediments are highly contaminated with heavy metals such as arsenic, cadmium, and lead. Many research projects are going on to find out the source of the contamination, to evaluate the toxicities to ecosystem, to estimate the volume of sediment to be treated and to find out a good remediation method. Reports show that the sediment is highly contaminated and the main contamination source is supposed to be abandoned mines and a zinc refinery located upper stream of the river. A magnetic separation has been tested as a treatment method for the dredged sediment. Lab scale test showed that the magnetically captured portion is about 10% in weight but the contamination of heavy metal is much higher than the contamination of the passed portion. This indicates that a magnetic separation could be applied for the purpose of reduction of sediment to be treated and for increasing the volume of low toxic sediments which can be dumped as general waste. A magnetic separation using a HGMS has been tested for the sediment with variable magnetic field and the results showed the higher magnetic field increase the captured portion but the concentrating effect of heavy metal was weakened. Further study is needed to establish a useful technology and optimization between decontamination and reduction of sediment volume.

Keywords: sediment, heavy metal, remediation, environmental application, magnetic separation

1. INTRODUCTION

Water resources were not enough for drinking water, industrial needs and agricultural purposes since most of the rainfall is in summer season causing flooding in summer and droughts in spring and winter in Korea. Therefore, several dams have been constructed for controlling flood and conserving water resources. Andong-dam is a multipurpose dam located in upstream of Nakdong river. This dam covers a huge watershed with an extension of 400.7 km^2 and storage capacity is 1.25 billion ton. The water quality of Andong-dam has been good for big downstream cities' water use. However, recent survey for the stream sediments over the country showed that the sediments of Andong-dam are highly contaminated with some heavy metals such as arsenic, cadmium, and lead. There is no big industry which might release contaminants but agricultural activities in the watershed of Andong dam. However, a zinc refinery and more than 50 abandon mines are located upstream as suspected pollution source. Most of the mine had been developed since Japanese colony during 1930s-1940s. The mines were abandoned until 1990s when Korean government started mine reclamation. In 2017, more than 17 thousand fish had died in Andong-dam and nongovernmental organization pointed the sediment contamination as cause of the massive death of fish but there is no evident directly connecting between sediment contamination and death of fishes. However, the contamination of sediments and massive death of fish have been an environmental concern. Several research and survey projects related with the sediment contamination are going on including the identification of the contamination resource and characterization of the contamination. Preliminary studies showed that the thickness of the sediment is more than 1 m which is accumulated during last 50 years and very fine particles are main constituents. Korean central government and K-water have tried to reduce environmental risk from the contaminated sediment. The ecological risk can be transferred to human through a few routes. Several treatments can be considered including capping and dredging of the contaminants sediments. Capping is relatively simple method covering the surface of sediments to protect release of heavy metal ions into water phase but this is not a permanent treatment [1]. To remove the risk by the heavy metal in sediments, dredging could be a preferred alternative but this method requires usually high cost and safe treatment of the dredged sediment. The amount of the dredged sediments will be several million tons and separation of the heavily contaminated sediments from less contaminated portion is a very necessary process for

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cost saving and environmental protection [2]. A conventional process is soil washing in which fine particles could be separated from coarse ones and usually fine particles contain more contamination due to the large specific surface area of fine particles and contaminants adsorbed on the surface. If the main contamination source is the mineral from mines, the heavy metal would be inside of the mineral and the particle size could not be a critical factor in determination of contamination level. Other processes, which could separate highly contaminated minerals came from abandoned mines or refinery out of background mineral particles, are needed. Magnetic separation can be tried for the separation process because the characteristics of minerals might be different due to the source of minerals. There are a few similar studies showing magnetic separation could enrich metals such as nickel and copper versus iron [3-5]. Rikers et al. reported heavy metal recoveries from soil using high intensity magnetic separation [6]. The objective of this study is to separate highly contaminated sediments from less contaminated portion by magnetic separation and to reduce the volume of sediment to be treated as hazardous waste.

2. EXPERIMENTAL METHODS

2.1. Chemicals

Heavy metal standard solution (1,000 mg/L) was purchased from Kanto Chemical and used for analysis. Nitric acid, sulfuric acid, and hydrochloric acid were obtained from Merck. All chemicals were used without further purification.

2.2. Analytical Methods

The sediments were analyzed for the heavy metal contents with ICP-MS (7800, Agilent). Analyzed species were As, Cd, Cr, Cu, Fe, Hg, Mn, Pb, and Zn. Magnetic property of the sediment was analyzed by a VSM (Model 7404, Lake Shore Cryotronics, Inc.). The accuracy and precision of the analysis of heavy metal were verified against certified reference samples (BAM-U112a). The particle size distribution of passed and captured sediment through magnetic separator was analyzed with a particle size analyzer (Mastersizer 2000, Malvern).

2.3. Sampling of the sediment from Andong dam

Contamination level of the sediment was evaluated by analyzing sediment samples collected from the dam. One sample at every 5 km from the dam was sampled and total 9 representative samples collected. The sampling sites were marked in a map of Fig. 1. For magnetic separation, samples from L3, L5, and L7 were used.

2.4. Magnetic Separation

A HGMS system equipped with a 6-Tesla cryo-cooled Nb-Ti superconducting magnet was employed.

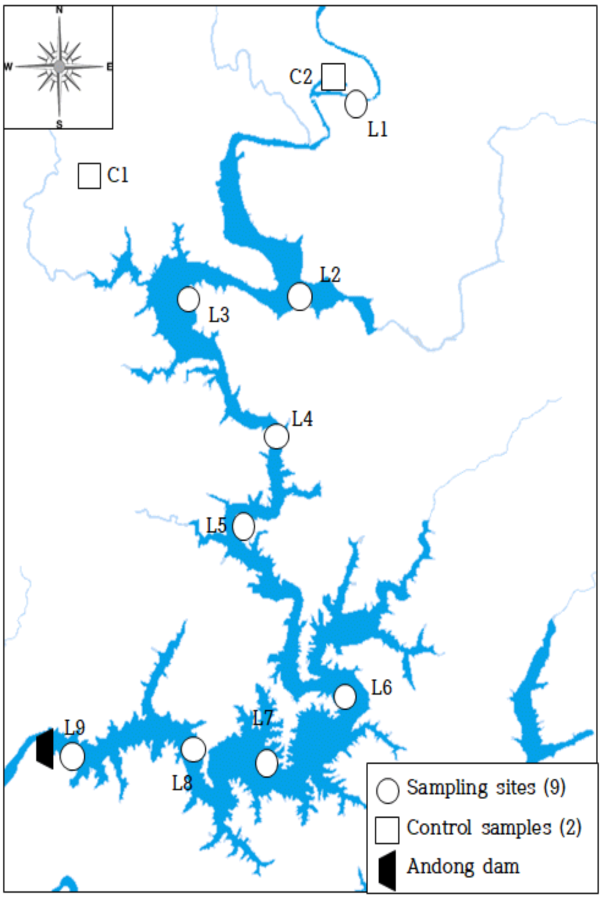

Fig. 1. Sampling sites in the Andong-dam area.

The bore size of the magnet was 100 mm in diameter and an acryl pipe was fitted into the bore as a sample channel. The magnetic filter was stainless steel mesh and the meshs were placed into the acrylic pipe. The magnetic filter size and interval were 10 mesh (0.254 mm) and 10 mm. The diameter of stainless steel wire is 0.3 mm.

Sediment particles could be caught by the magnetic moment generated per unit volume of the sediment particle. The magnetic force in the particles is given by following equation [6]:

$$F_m = (1/\mu_0)\rho\chi VB\nabla B \quad (1)$$

Where μ_0 is permeability in vacuum ($4\pi \times 10^{-7}$) (H m^{-1}), χ is the specific magnetic susceptibility (m^3/kg), ρ is the specific gravity (kg/m^3), V is the volume of particle (m^3), B is magnetic induction (T).

The magnetic separation experiments were conducted in batch tests. The sediment was suspended into distilled water and the solid/liquid ratio was 1:10. The prepared sediment slurry was introduced into the acrylic pipe fitted in the bore of the HGMS. The caught sediment particle on the steel mesh was collected by removing the pipe and steel mesh from the bore after each set of experiment. The separation experiments were repeated in variable magnetic field ranged from 1.0 T to 6.0 T.

The flow velocity of slurry was 0.20 m/min.

3. RESULTS AND DISCUSSION

3.1. Volume reduction of the sediment

Evaluation of sediment from Andong-dam showed that the sediments highly contaminated. Total nine heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Zn) were analyzed and two metals (As, Cd) resulted in Korean sediment contamination level IV which is the highest contamination level meaning very high possibility to have toxic effect on benthic organisms. Three metals (Hg, Pb, Zn) showed contamination level II which indicate a moderlate possibility of toxic effect on benthic organism. The contamination was widely spread over the dam through about 40 km length. However the iron content was about 3-5 % showing magnetic separation might works by the iron minerals.

TABLE I
CIRERIA FOR EVALUATION OF THE CONTAMINATION LEVEL FOR DAM SEDIMENT. (NATIONAL INSTITUTE OF ENVIRONMENTAL RESEARCH, KOREA, 2015) (mg/kg)

Level	Cr	Ni	Cu	Zn	As	Cd	Pb
I	≤ 112	≤ 53	≤ 60	≤ 363	≤ 29	≤ 0.4	≤ 65
II	≤ 224	≤ 87.5	≤ 228	≤ 1170	≤ 44.7	≤ 1.87	≤ 154
III	≤ 991	≤ 330	≤ 1890	≤ 13000	≤ 92.1	≤ 6.09	≤ 459
IV	> 991	> 330	> 1890	> 13000	> 92.1	> 6.09	> 459

TABLE II
CONCENTRATION OF HEAVY METALS BEFORE MAGNETIC SEPARATION. (mg/kg)

Classify	Cr	Ni	Cu	Zn	As	Cd	Pb
Up stream	34.3	24.1	48.6	764.2	83.1	12.6	142.2
Mid stream	29.3	24.4	42.3	423.3	94.3	8.2	101.3
Down stream	50.0	41.4	60.3	644.9	104.9	8.0	138.3

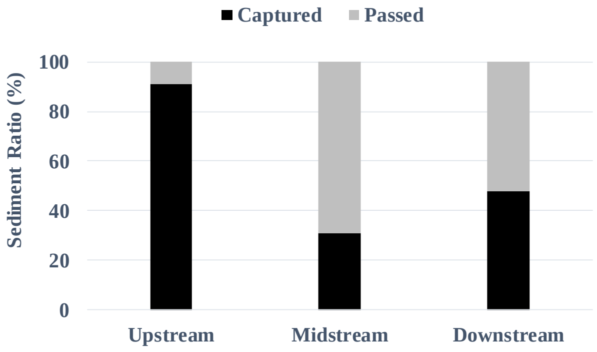

Fig. 2. The ratio of captured to passed sediment tested at 1.0 T of magnetic field.

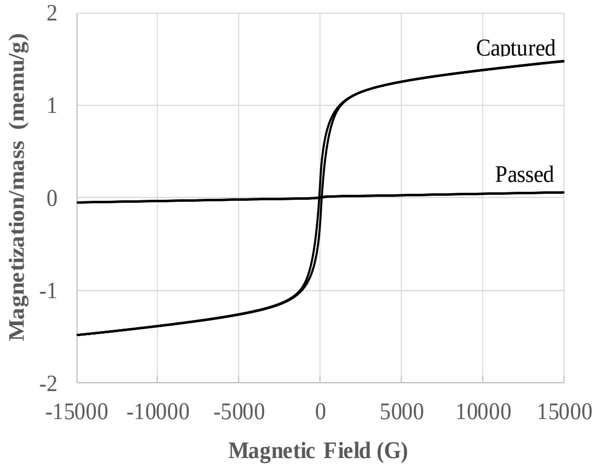

Fig. 3. Magnetic properties of the captured and passed sediments.

Fig. 2 showed that the ratio of captured to passed sediment through the magnetic separation device. In case of the upstream sample, most of the sediment was captured even at the 1.0 T of magnetic field. However, the passed portion increased for the midstream and downstream sediments indicating the magnetic properties of sediment is related with the sedimentation environment. In general, the captured ratio increased with magnetic field. Current results showed that variable magnetic field is needed depending on the separation ratio of the sediment. Particular difference was not observed in the particle size distribution of the captured and passed ones except downstream one which showed passed sediments were finer than that of captured.

Magnetic properties of passed and captured sediments were analyzed with a VSM and the result is showed in Fig. 3. The captured sediments has a weak saturation magnetization (M_s) and coercive force (H_c) but the passed sediments showed negligible magnetic properties indicating some particle can be separated and others cannot in the particle mixture of sediment.

Table II showed the contamination level of sediment before the magnetic separation. Table III showed that concentration of heavy metal in the passed sediment and captured one after magnetic separation. In case of upstream sediment, cadmium and arsenic enriched in captured portion resulting in contamination level improved from level III to level I for arsenic and from level IV to level III for cadmium. In chromium, zinc, and lead, similar trends was observed. The concentrating effect is slightly proportional to the magnetic field with higher magnetic field giving somewhat higher enrichment. There are a few exceptions such as chromium and nickel for midstream and downstream, in which case the metals were concentrated in passed portion. Current results indicate that simple magnetic separation can reduce the volume of sediments to be treated intensively by collecting highly contaminated one out of less contaminated one.

TABLE III
CONCENTRATION OF HEAVY METALS AFTER MAGNETIC SEPARATION. (mg/kg)

Classify		Magnetic Field (T)	Cr	Ni	Cu	Zn	As	Cd	Pb	Fe
Up stream	Captured	1.0	41.2	8.6	23.7	435.1	38.9	6.6	100.6	33174
		3.0	25.9	5.7	25.5	460.4	44.9	6.6	103.2	37702
		6.0	128.3	43.3	33.1	475	58.8	8.8	105.2	38798
	Passed	1.0	14	0	33.6	303	43	4.8	62.4	5077
		3.0	20	0	17.5	224.3	28.1	5.8	64.7	16555
		6.0	7	0	7.4	116.4	13.1	2.3	55.6	18781
Mid stream	Captured	1.0	29.5	7.8	13.9	246.4	46.5	4.3	90	26536
		3.0	31.1	0	20.5	374.8	66.1	6	85.4	31071
		6.0	22.4	6.5	20.8	415.8	67.5	6.2	101	34689
	Passed	1.0	17.5	3.9	16.3	317.6	54	5.1	90.1	23783
		3.0	14.9	18.6	19.4	284.6	51.6	5.7	83.8	20401
		6.0	230.6	196	18	163	22.1	3.3	53.7	14189
Down stream	Captured	1.0	21.2	6.7	20.6	370.2	55.9	5.3	115.5	31955
		3.0	31.8	9.1	23.8	442.4	59.6	5.2	121.3	35943
		6.0	40	10.9	26.6	452.5	62.7	6	143.8	35557
	Passed	1.0	14.5	124.5	56	377.4	44.7	3.7	113.9	30356
		3.0	26.5	49.8	28.6	330.3	43	3.6	104.3	28752
		6.0	24.1	10	0	266.6	41	3.9	53	22494

T : Unit of Magnetic Field

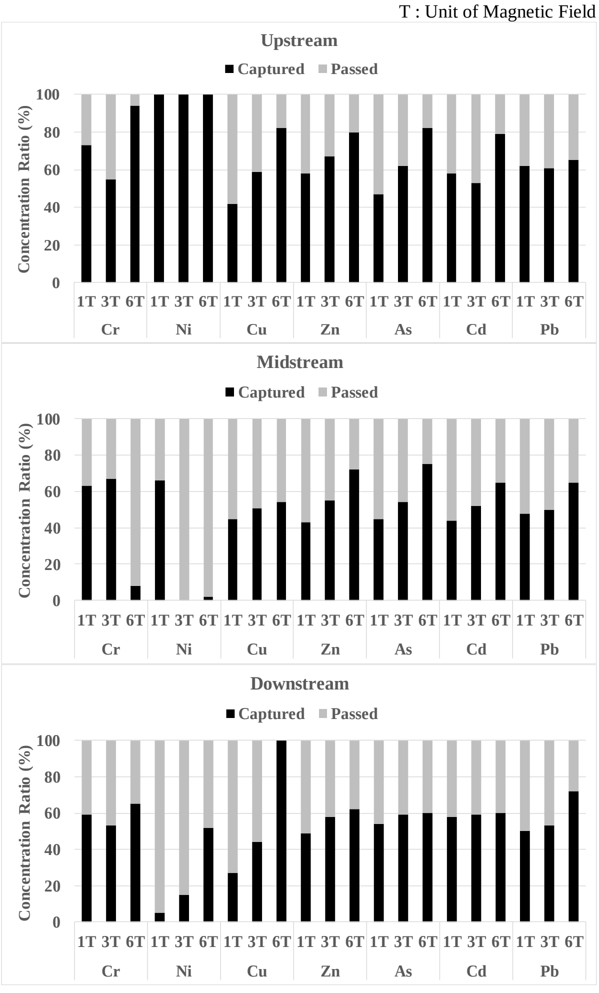

Fig. 4. Comparison of the concentration ratio between the captured and passed portion.

The concentration ratio of heavy metal species were compared upon the magnetic field and sampled location in Fig. 4. For upstream sediment the ratio was affected by the magnetic field density with increasing captured ratio at higher magnetic field. The increase of the ratio upon the increase of magnetic field was similar in midstream sediment but a few metal species such as chromium and nickel showed reverse phenomena. This indicates the composition of sediment could be different with the settled location. The particle size and density of the sediments are variable depending on the settled location with bigger particles and dense ones settled in a upstream area while finer particles usually settled in a midstream and downstream area. The sedimentation environment could affect the mineral composition.

The correlation between the concentration of each element and the magnetic separation efficiency was shown in Fig. 5. The plot shows some metal have relatively high correlation. Especially, Cu, Zn, Cd, and Fe have 0.8 of coefficient or higher indicating as the captured ratio increase, the concentration of those metals increase. However, Pb, Ni, and Cr shows the correlation coefficient ranged from 0.28-0.47 indicating moderate correlation. For As no correlation was observed indicating the efficiency of separation was not proportional to the concentration of arsenic.

4. CONCLUSION

The application of magnetic separation has been expanded into many areas and the current application is for the volume reduction of contaminated sediments. Sediment of Andong-dam turned out highly

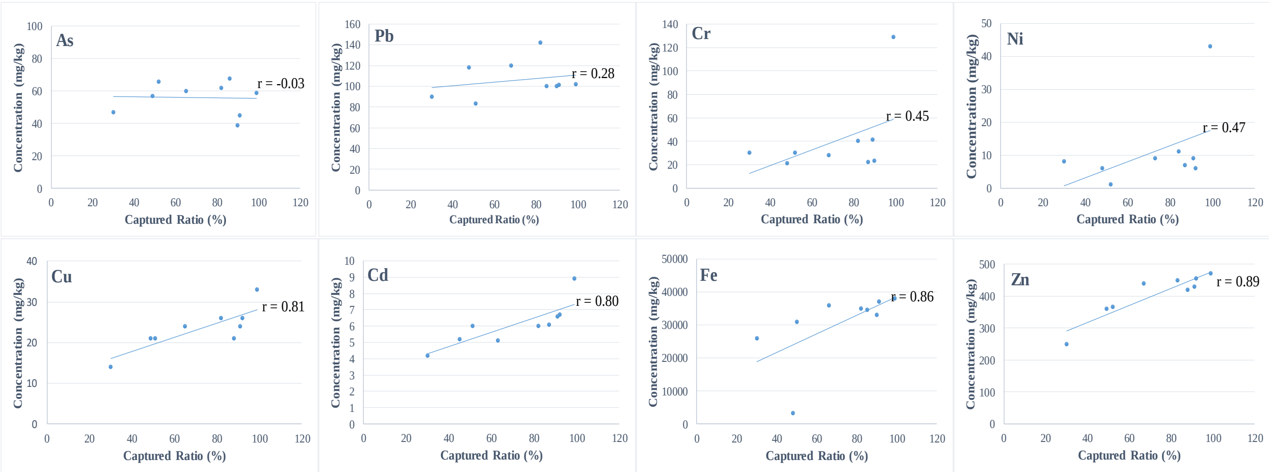

Fig. 5. Correlation analysis between heavy metal concentration and the magnetic separation efficiency.

contaminated with some heavy metals and the source of contamination is under investigation. A HGMS was tested for the contaminated sediment slurry and the magnetic separation concentrated heavy metal usually in magnetically captured portion giving passed one has relatively low contamination. This process eventually can reduce the volume of sediment to be intensively treated as hazardous waste. Less contaminated sediment can be used as soil for construction and agricultural purposes. The magnetic separation efficiency was depends on the magnetic field and characteristics of the sediments. The location of sedimentation also affected on the efficiency. Current study proved that a HGMS can be applicable to contaminated sediment.

ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MOE) (NRF-2017R1D1A1B04036516).

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