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Distribution and Mobility of Heavy Metal Materials in Settling Ponds Post Laterite Nickel Mining (A Case Study: North Motui Konawe, Southeast Sulawesi)

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ABSTRACT
The formation of waste matter sedimentation in settling ponds, along with accumulation of heavy metals, such as Nickel (Ni), Chrome (Cr^{3+} and Cr^{6+}), manganese (Mn) and Cobalt (Co) and elements or compounds in laterite soil. These heavy metals will concentrate in different environmental geochemistry, which are laterite sediment layers pre- and post-mining. The purposes of this study are to identify changes of heavy metal distribution in settling ponds and analyze heavy metal mobility in settling ponds. The research methods were qualitative and quantitative methods. Laboratory research used AAS (*Atomic Absorption Spectrophotometer*) which was studied, analyzed, and synthesized comprehensively. Data processing technique used SPSS v.21 software and Principal Component Analysis (PCA) method. The result showed that distribution of heavy metals Fe and Cr relatively strengthened constantly. The graphs of Fe and Cr were interpreted as similar mobility and mechanism of transportation os elements which can form chemical compounds. Meanwhile, metals Ni and Co had similar graph which was relatively flat constantly. This was interpreted as similar mobility of heavy metals in settling ponds. The mobility of heavy metals Fe and Cr were mostly concentrated to form *ferrochrome* compound in the sediment of settling ponds compared with Ni with its low mobility and Co with its very low mobility.

Keywords - Atomic Absorption Spectrophotometer (AAS), Heavy Metal, Principal Component Analysis (PCA), Settling Pond

I. Introduction

1.1. Background of the Problem

The formation of waste matter sedimentation in settilng ponds, along with accumulation of heavy metals, such as Nickel (Ni), Chrome (Cr^{3+} and Cr^{6+}), manganese (Mn) and Cobalt (Co) and elements or compounds in laterite soil. These heavy metals will concentrate in different environmental geochemistry, which are laterite sediment layers pre- and post-mining. Post-mining, the sediment of laterite nickel, heavy metal in the soil become unstable and is environmental geochemistry disturbance. Geochemical disturbance can also happen in holes created by mining with will be filled with water (rain, overflowing rivers or seas) if not covered or reclaimed, creating lakes or large ponds. Pits of former mines are unique habitats because they're generally narrow and surrounded by steep walls of rocks. Environmental geochemistry disturbances are accumulations of heavy metals due to changes of water concentrations in sediments such as pH, Eh, ion property, concentration type, metal bond and size distribution [1]. Sediments consist of several components and many are combinations of components in a particular area. The components vary depending on location, depth and basic geology [2].

Open mining impact laterite nickel sediment management which strongly influences environmental geochemistry disturbances in the area due to mining. Today, there are 26 mining companies which manage exposed laterite nickel metallic mineral in North Konawe Regency, Southeast Sulawesi Province, including Motui area [3]. Layers which don't contain economic ores are placed in areas called waste material storages. Waste material storage areas are connected to settling ponds to store the flow of surface water. When heavy metals enter sea environment, the heavy metals will be distributed through water columns, stored or accumulated in sediment and consumed by organisms [4].

1.2. Research Purposes

This study has the following purposes:

- To identify changes of heavy metal distribution in settling ponds.

- To analyze mobility of heavy metals in settling ponds.

II. Theoretical Basis

Settling ponds are an integral part of a mining process where aggregation separation takes place [5]. The study by Vinten *et al* concludes that heavy metals in the sediment of settling ponds depend on the sources, e.g. nickel (2 to5300 mg/kg); chrome (10 to 99.000 mg/kg) [6].

A settling pond consists of three parts, which are inlet zone, settling zone, sludge zone and outlet zone. Entry mechanism of waste materials in settling ponds is following water flow (inlet zone), then coarse waste materials will be precipitated (settling zone). After coarse materials are precipitated, fine materials follow water flow and form Total Suspended Solid (TSS) which is precipitated in the sludge zone, then water exits settling ponds (outlet zone) [7].

Heavy metals are component created in nature or on earth crust and don't experience degradation or aren't destroyed. The term heavy metal is based on a mtal chemical element which have relatively high density (density above 5 g/mL) and contains toxic although in low concentration, for example arsenic (As, cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and thalium (Tl) [6]. Metal concentration in water is relatively slow and forms layers in sediments. Metal accumulation from water and are precipitated depends on factors such as pH, ionic strength, type and concentrations of organic and anorganic bonds (anthropogenic input), surface variation of sediment due to distribution of grain size [8].

Heavy metals such as Ni, Cr, Fe, Mn from ultrabasic rocks, laterite soil, and sediments will have different geochemical properties [9]. Geochemical mobility of elements depends on acidic environment or the increase of the influence of acid. This makes non-crystalline metals form fractions in sediments, for example: Mn, Zn, Cd, Co, Ni. Change of reduction condition into oxidation includes transformation of sulfide in more acidic condition. This will increase the mobility of "chalcopilic" type elements which are Hg, Zn, Pb, Cu and Cd. In other words, the lowest mobility characteristic is in Mn and Fe in oxidation condition [10].

III. Research Method

The research methods were qualitative and quantitative methods and petrography and mineragraphy laboratory research by AAS (*Atomic Absorption Spectrophotometer*) which was studied, analyzed, and synthesized comprehensively. Data processing technique used SPSS v.21 software and Principal Component Analysis (PCA) method. The population in this study was heavy metals which were in settling ponds and associated with clay. Sample collection from settling ponds were taken from 12 points and 4 elements of heavy metals which were Ni, Fe, Co, Cr were collected.

Sample collection of suspended material used PVC pipes with 3 cm diameter. Sample collection was performed systematically in settling ponds. PVC pipers were pressed vertically until the depth of approximately 20 cm to 30 cm or clay sediment layer limit.

VI. Result and Discussion

4.1. Research Result

Table 1. Result of Research of Sediments in Settling Ponds

No.	Sample I.D	Metals (mg/dryKg)			
		Chromium (Cr)	Cobalt (Co)	Iron (Fe)	Nickel (Ni)
1	MM 1	1360	357	135000	9980
2	MM 2	1870	299	174000	12500
3	MM 3	2350	356	180000	12400
4	MM 4	2950	255	199000	11500
5	MM 5	3080	321	217000	12400
6	MM 6	2970	271	203000	12100
7	MM 7	3110	296	208000	12800
8	MM 8	2920	356	209000	11700
9	MM 9	2980	366	203000	12000
10	MM 10	3210	290	204000	13000
11	MM 11	2990	294	199000	11600
12	MM 12	2900	280	185000	13300

4.2. Distributions of heavy metals in settling ponds

Difference of heavy metal contents in settling pond was interpreted as accumulation of elements which were transported from ultrabasic rocks. Fig.1 shows that the graphs of heavy metals Fe and Cr relatively strengthened constantly. The graphs of Fe and Cr were interpreted as similar mobility and mechanism of transportation of elements which can form chemical compounds. Oxidation process dissolved Fe so that in acidic water and precipitation it formed ferrihydrite mineral. This process always happened at sedimentation phase of clay mineral so that the composition of Fe was discovered as $Fe(OH)_3$ as ferrochrome (Fe Cr_2O_3) [11]. Meanwhile, metals Ni and Co had similar graph which was relatively flat constantly. This was interpreted as similar mobility of heavy metals in settling ponds. Metal concentration in water was relatively slow and formed layers in sediments [8]. Heavy metal Ni has very low mobility in alkaline – neutral condition if proton activities take place in precipitation condition with clay [12].

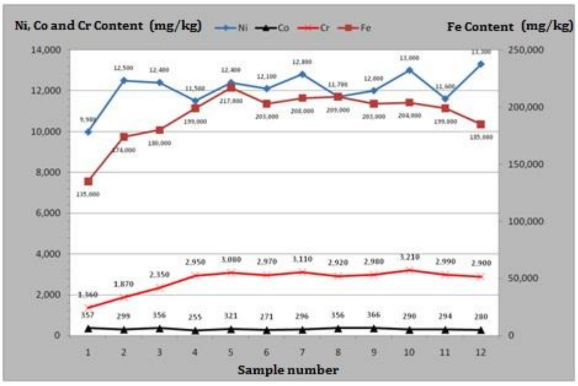

Fig.1. concentration pattern of heavy metals in settling ponds

4.3. Mobility of heavy metals in settling ponds

Communality values showed variation which could be explained by formed factors. These values were obtained by squaring correlation values from matrix components. Table 2 shows that the value of nickel variable is 0,109 or 10,9%, so as a variable nickel could be explained by form factors of heavy metals Fe, Cr and Co. Communality value of Fe is 0,944 or 94,4% so Fe variable could be explained by form factors of heavy metals Co (0,918 or 91,8%) and Cr (0,920 or 92 %).

Communality values showed that changes of heavy metal Ni from ultrabasic bedrocks and settling ponds were relatively weak (0,109), while heavy metals Fe, Co, Cr were relatively strong. Change of heavy metal Ni showed that the release of ultrabasic rock elements happened earlier in Ni, then followed by Fe, Co and Cr. The release of elements is generally caused by difference of mobility influenced by radius of ions and hydrolysis condition [12]. Degree of mobility depends on heterogeneity of ultrabasic protolith and the formation of allogeneic minerals. The higher average degree of mobility is Ca>Mg>Si>Ni>Co~ Zn~V>Fe = Cr ~ Mn [13].

Table 2. Communality values of heavy metals

	Initial	Extraction
Ni	1	0.109
Fe	1	0.944
Co	1	0.918
Cr	1	0.92
Extraction Method: Principal Component Analysis.		

Analysis of total variance in the result of heavy metal Ni has the biggest eigenvalue which is: 2,892 which is 72,289% of tr(R). Meanwhile heavy metal Fe has the biggest eigenvalue which is: 2,892 + 0,928 from 95,486% of tr (R). Heavy metal Co has the biggest eigenvalue which is: 2,892 + 1,362 + 0,123 from 98,552 (Table.3). After knowing eigenvalues, there were values with loading factors which were interpreted as metals with strong influence on rocks and settling ponds. Distributions of heavy metals Ni, Fe, Co had relatively big influences on ultrabasic bedrocks and settling ponds, as follows : Ni > Fe > Co.

Table 3. The value of total variance explained

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	**% of Variance**	**Cumulative %**	**Total**	**% of Variance**	**Cumulative %**
Ni	2.892	72.289	72.289	2.892	72.289	72.289
Fe	.928	23.197	95.486			
Co	.123	3.066	98.552			
Cr	.058	1.448	100.000			
Extraction Method: Principal Component Analysis.						

This heavy metal composition illustrates that Ni ultrabasic rock is very reactive in releasing elements which contain Fe, forming oxidation. Heavy metal Cr has very small eigenvalue factor and large cumulative score, showing that heavy metal chrome has different distribution property than the three heavy (Ni, Fe, Co) in ultrabasic bedrocks and settling ponds. Relatively high value in heavy metal chrome (Cr) was interpreted as relatively stable sedimentation in settling ponds relatively small influence of surface water.

Table 4 shows loading factors (correlation values) between analysis variables and formed factors. It shows that only Fe has the highest score (0,972), indicating that Fe could be reduced by heavy metal Ni, but was relatively weak on Co and Cr. Similar loading factors in Co and Cr show that both elements couldn't reduce each other and had different influences on Fe. It's interpreted that heavy metal chrome was precipitated well in settling ponds and followed by sedimentation of heavy metal Co which was influenced by heavy metal Fe from the flow of surface water.

Fig. 2 shows Ni, Fe, Co, Cr located in the same component which was component 1 and was an illustration of accumulation of distributions of heavy metals in settling ponds. Heavy metal Ni relatively formed single populations which were interpreted as low mobility in reduction condition of settling ponds. There was similarity between Ni and Cr in that heavy metal Cr would have limited mobility if Ni level increased, and this generally happens in iron oxide layers [12].

Table 4. Loading factor value of each Heavy Metal

Logam Berat	Component
	1
Ni	.331
Fe	.972
Co	.958
Cr	.959
Extraction Method: Principal Component Analysis.	
a. 1 components extracted.	

Meanwhile, in heavy metals Co, Fe, Cr formed multiple population which was interpreted as similar very low mobility in reduction condition, neutral to alkaline with water and sediment media. Cr populations showed slices containing Fe which was interpreted as an illustration of similar very low mobility oxidation and neutral-alkaline conditions. Very low mobility condition is elemental geochemical mobility which depends on acidic environmental and causes non-crystalline metals to form fractions in sediments [10]. This condition is characterized is by color change of soil from reddish to blackish which shows accumulation of heavy metal iron along with the dissolution of surface water. The condition of Cr was very stable and resistant to materials from reformed ultrabasic rocks, but Ni was very unstable. Heavy metal Fe in sediments was influenced by clay mineral and low temperature, forming Fe-hydroxides. Fe and Cr in sediments would form ferrochrome compound where electron activities changed into proton [12].

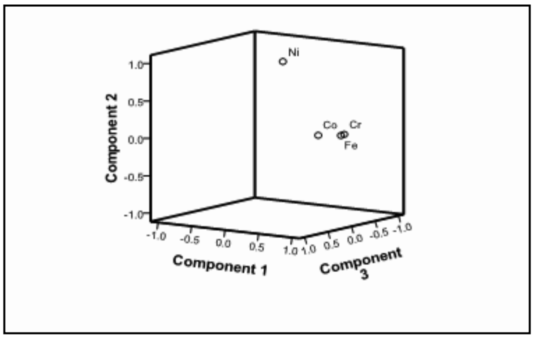

Fig.2. Mechanism of changes of distributions of heavy metals in settling ponds

V. CONCLUSIONS

The conclusions drawn are:

- Distributions of heavy metals Fe and Cr relatively strengthened constantly. The graphs of Fe and Cr were interpreted as similar mobility and mechanism of transportation of elements which can form chemical compounds. Meanwhile, metals Ni and Co had similar graph which was relatively flat constantly. This was interpreted as similar mobility of heavy metals in settling ponds.
- The mobility of heavy metals Fe and Cr were mostly concentrated to form *ferrochrome* compound in the sediment of settling ponds compared with Ni with its low mobility and Co with its very low mobility.

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