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THE RELATIONSHIP OF ULTRAMAFIC ROCKS AND THE OCCURRENCE OF ARSENIC HEAVY METAL ION (AS^{3+}) CADMIUM (CD^{2+}) AND CHROMIUM (CR^{6+}) IN RIVER WATER

(A Case Study: River Lambuluo Motui, Southeast Sulawesi)

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Abstract: The research objective was to analyze the relationship between constituent minerals of ultramafic rocks as bedrocks carrying nickel elements towards the occurence of cadmium and chromium arsenic metal ions in rivers surrounding mining areas, especially in the region of Motui, North Konawe, Southeast Sulawesi Province. The research was observational method, i.e. direct survey data collection in the field, both river constituent water samples and rocks samples of the research site. Furthermore, the samples were analyzed by Atomic Absorption Spectrometry (AAS) and petrography and mineragraphy. The type of constituent Utramafic rock of the research site is peridotite and contains mineral Chromite ($Fe_2Cr_2O_4$) and Nickelline (NiAs). Meanwhile, the occurrence of arsenic metal ion, cadmium and chromium in the research site has exceeded the stipulated quality standards.
Keywords: nickel, ultramafic, heavy metals, Atomic Absorption Spectrometry.

Introduction

Nickel mining in Motui District located in Mount Lamotia with the mining area of 439.5 Ha. River Lambuluo exists surrounding this mining area, which is the location of mining waste disposal. This river has undergone turbidity even during heavy rain, the river water changes into reddish in color. It is because the soils derived from mining activities are carried by rainwater downward the river. Heavy metals entering into the river will be carried away to wider waters, and if will be hazardous to health whenever consumed in excessive quantities (Darmono, 2006). The analysis results of the Kendari Environmental Agency in April 2012, it is determined that metal concentration contained in water and sediments samples in the residents ponds surrounding nickel mining in Motui District have been contaminated by metals Ni, Pb, and Cd. The concentration of these metals has exceeded the threshold stipulated by the government, i.e. in accordance with Decree of Environment Minister Number 51 of 2004 on Sea Water Quality Standard for Marine Biota. Nickel mining, besides

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producing nickel minerals, it also produces other heavy metals associated with other molecules forming complex compounds. Nickel mining produces other heavy metals, such as As, Cu, Fe and etc (Ahmad, W. 2006).

Data and Methodology

The research was conducted in May-June 2013, located at River Motui, Lambuluo District, North Konawe Regency, Southeast Sulawesi Province. The samples in this research were the water and the rocks, taken at each research station. The water sample was taken at 3 points and be repeated as many as 3. For a period of three days with time interval among the first, the second and third day taking had time gap of 1 day. Later on, they were analyzed using Atomic Absorption Spectrometry (AAS) tool.

Meanwhile, the rock samples taken on the bed rock or fresh rocks were on 13 points. Furthermore, it was analyzed by the mineralogy of ultramafic rocks using petrography and mineragraphy.

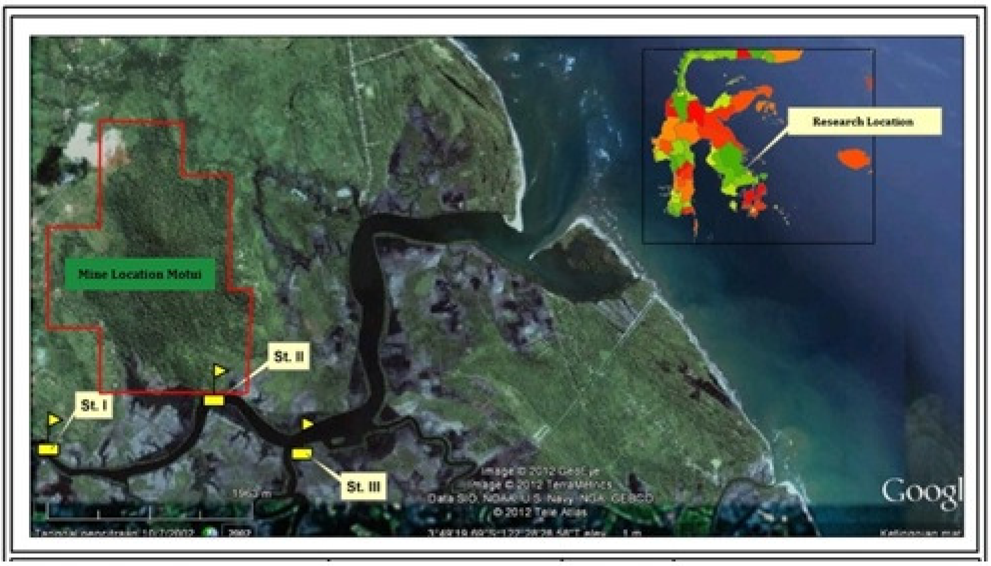

Figure 1. Location Map and Points of Water Sampling Station

Results and Discussions

A. Condition of Ultramafic Rock Mineralogy of Constituent Laterite Nickel

Table 1. Petrography Analysis Result

Mineral Composition	Sample Number												
	IQ-A2	**IQ-B1**	**IQ-B3**	**IQ-B4**	**IQ-B5**	**IQ-A1**	**IQ-A5**	**IQ-B2**	**IQ-A3**	**IQ-A4**	**IQ-A6**	**IQ-A7**	**IQ-A8**
Primary Minerals	%	%	%	%	%	%	%	%	%	%	%	%	%
Olivine	40	25	35	35	35	15	10	35	15	20	20	25	30
Pyroxene	20	20	25	25	35	15	10	20	25	15	15	0	20
Plagioclase	0	0	0	0	0	0	0	0	5	0	0	0	0
Glassy	25	45	20	20	15	10	15	35	35	40	40	45	25
Secondary Minerals													
opaque	5	5	10	5	5	5	10	5	10	10	5	5	5
Serpentine	10	5	10	15	15	40	60	15	10	15	5	10	15
Quartz	0	0	0	0	0	5	0	0	0	0	15	15	5
Total	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**
Rock Name	**Peridotite**					**Serpentinite in Peridotite**			**Wheathering in Peridotite**				

Source: The Sampling in the Research Site

Peridotite field appearance found on stations A1, A2, A3 and A8 commonly show fresh brownish green in color produced from dominant mineral composition, and in a state of weathered brown in color, crystallinity hipokristalin texture, granularity faneroporfiritik, subhedral - anhedral fabric form, inequigranular relation, massive structure, formed by the olivine mineral, piroksin and basic mass. Generally, rocks found above the station has undergone serpentinization process, thus indicating the presence of the mineral serpentine. Based on the physical characteristics and mineral content, thus the name of these rocks is Peridotite (Travis, 1955).

The rocks incision is brownish white. The texture is consisted of crystallinity hipokristalin, granularity faneroporfiritik, inequigranular relations, subhedral - anhedral mineral form, mineral composition, consisted of primary mineral, i.e. 15% olivine, 25% piroksin, 5%plagioclase, 10% opaque mineral, 35% basic mass, and alteration mineral, i.e. are serpentine. The intensity of alteration in the rocks' incision is classified as moderate for amount of serpentine mineral reaches 5-10% out of the rocks' total volume. The alteration pattern is included in selectively pervasive because only certain minerals which may alter. The name of rocks: Peridotite (Strekeisen, 1974).

Figure 2. Ultramafic Rocks of the Research Sites

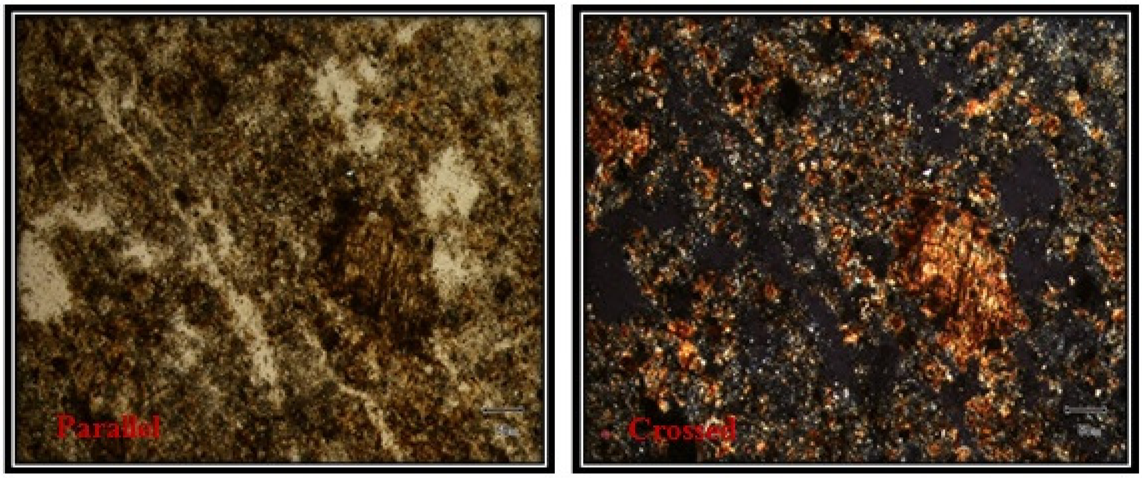

Figure 3. Petrograph of Ultramfic Rocks in the Research Sites

Color: Greyish orange; Cleavage: Poor/Indistinct; Fracture: Uneven; Textures: Primary Growth Textures; Pleochroism: -; Anisotropism: Weak; Internal Reflections: Redish brown; Hardness: 5.5; Associated minerals: Nickelline and pyrite; Crystal System: Isometric Mineral: ***Chromite*** **($Fe_2Cr_2O_4$).** Color: Brown; Cleavage: Poor/Indistinct; Fracture: Conchoidal; Textures: Primary Growth Textures (Disseminate); Pleochroism:-; Anisotropism: Weak; Internal Reflections: -; Hardness: 5–5.5; Associated minerals: Chromite dan pyrite; Crystal System: Hexagonal; Mineral: ***Nickelline*** **(NiAs)** (James and David, 1981).

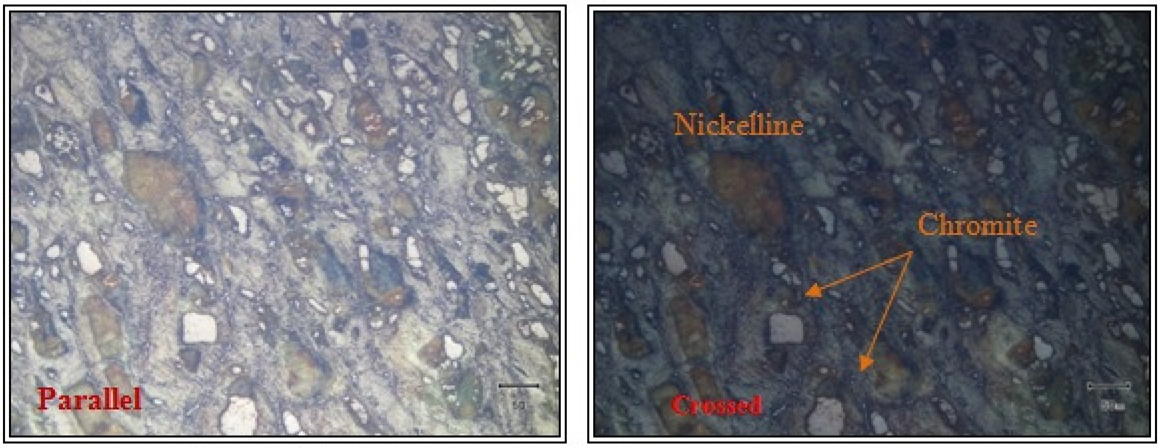

Figure 4. Incision Polished of Ultramfic Rocks of The Research Sites

B. The Condition of Metal Ion in River Water

The concentration of metal ions in Lambuluo's river water at each station has a sequence of AS^{3+}> Cr^{6+}> Cd^{2+}. The concentration of metal ions in the river water can be seen on the Table.

Table 2: ion concentration AS^{3+}, Cd^{2+} and Cr^{6+} in river water samples in River Lambuluo

No	Metal Ion	Station	Content (mg/L)			Quality standards
			Day I	Day II	Day III	
1	Arsen (As^{3+})	I	0	0,13	0,009	0,012
		II	0,2	0,15	0,1	
		III	0,2	0,18	0,15	
2	Kadmium (Cd^{2+})	I	0,002	0,004	0,001	0,001
		II	0,001	0,009	0,002	
		III	0,001	0,001	0,0014	
3	Kromium (Cr^{6+})	I	0,005	0,005	0,007	0,005
		II	0,001	0,0025	0,0018	
		III	0,001	0,003	0,003	

Description: Based on LH Decree No. 51 of 2004 on the sea water quality standard for marine biota.

A. Ion Arsen (As3 +)

Based on the analysis result, AS^{3+} ion concentration has exceeded the quality standards > 0.012 mg/L (Decree of Environment Minister No. 51 of 2004). AS^{3+} ion concentration in the river water on the first day of sampling is 0-0.2 mg/ L (Table 2), on the second day AS3 + ion concentration tends to be equal at each station, i.e. from 0.13 to 0.18 mg/ L, as well as on the third day with AS^{3+} ion concentration, ranged from 0.009 to 0.15 mg/ L. the increased concentration of AS^{3+} ion concentration in each sample is resulted from the high TSS and turbidity at stations II and III, thus affecting the AS^{3+} ion concentration. AS^{3+} ion content in River Lambuluo can be seen in Figure 5.

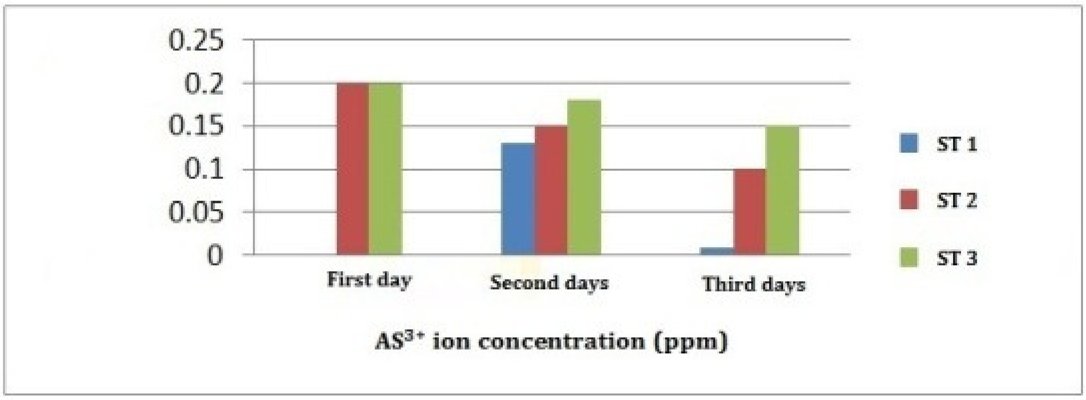

Figure 5. AS^{3+} ion concentration in river water at each station

B. Chromium Ion (Cr^{6+})

The analysis of Cr^{6+} ion concentration in the river water samples at first, second and third consecutive days is between 0.001 - 0.005, 0.002-0.005 and from 0.001 to 0.007 mg/ L. Cr^{6+} ion concentration at station I is greater than the concentration at stations II, and III on the first up to third day (Table 2). It is due to pH and salinity of the water at station I is lower than at stations II and III. It is consistent with the statement Hutagalung (1991); the decrease in salinity and pH and the rise in temperature may lead to the increased ion concentration in the water. Cr^{6+} ion concentration in River Lambuluo, North Motui Konawe District can be seen in Figure 6.

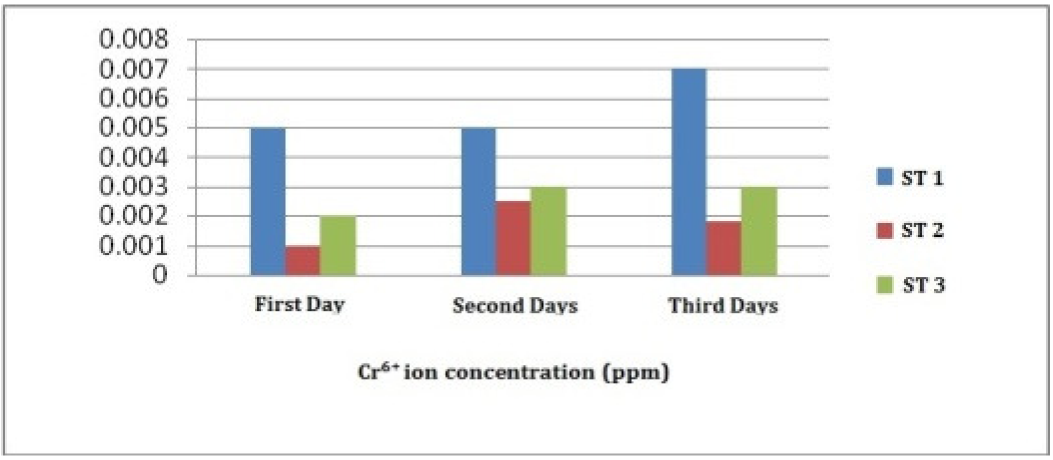

Figure 6. Cr^{6+} ion concentration in river water at each station

C. Cd^{2+}Ion

Cd^{2+} ion concentration in Lambuluo's river water on the first day at the stations I, II and III are 0.002, 0.001 and 0.0009 mg/ L, respectively, showing a relatively homogeneous distribution pattern. On the second day, Cd^{2+} ion concentrations of the stations are 0.004, 0.009 and 0.001 mg/ L, respectively. While on the third day, Cd^{2+} ion concentration value tends to be the same on each station (Table 2). The high concentration of Cd^{2+} ions in Lambuluo's river water is affected by physico-chemical factors of river water.

The degree of acidity or pH controls the solubility and metals concentration underwater. The relatively high pH conditions increases the occurrence of Cd^{2+} ion deposition, thus the Cd^{2+} ion concentration in the water is low. Based on the Decree of Environment MInister on sea water quality standards at the station I, it has passed the quality standards for marine biota, i.e. 0.001 mg/ L. According to Palar (1994), Cd^{2+} ion concentration in the water body with a concentration of 0.005 to 0.15 mg/ L within time interval of 24-504 hours may result in the death of crustaceans, and Cd^{2+} ion with a concentration of 0.003 to 18 mg/ L may result in death of insects. Cd^{2+} ion concentration in the river water can be seen in Figure 7.

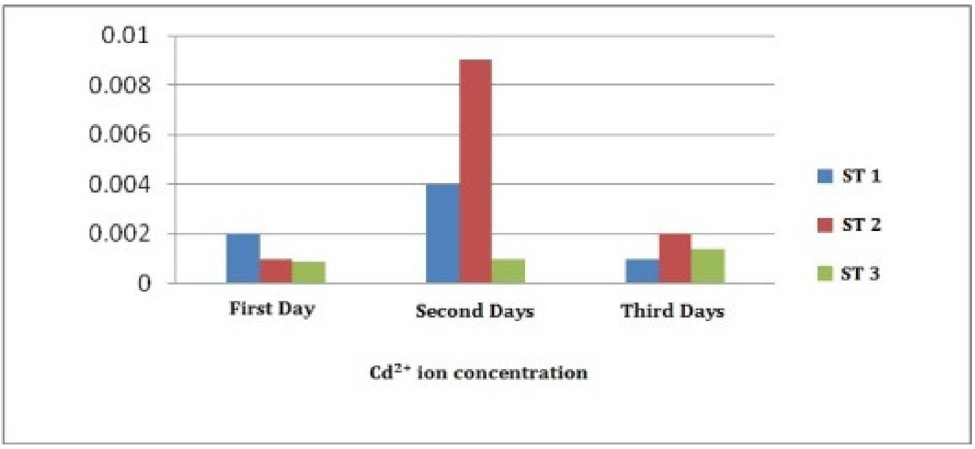

Figure 7. Cd^{2+} ion content in river water samples

D. The Relationship of Constituent minerals of Ultramafic Rocks on the occurence of Arsenic Heavy Metal Ion ($AS^{3+)}$ Cadmium ($Cd^{2+)}$ and Chromium (Cr^{6+}) in River Water

The presence of constituent minerals of ultramafic rocks are peridotite in the research area, in which the lithology contains more mineral olivine ($(Mg,Fe)_2SiO_4$) and piroksin, i.e. the type of ortho and klinopiroksin ((Ca, Mg, Fe, Na, Al, Ti) Si2O6). The corrosion process begins in peridotite ultramafic rocks, in which these rocks contain much olivine, piroksin, magnesium silicate and iron silicate minerals, which generally contains 0.3% Ni. These rocks are easily influenced by laterization weathering. Because the groundwater fluctuations which is rich in

CO_2, it will be in contact with the saprolite zone that still contain the derivation rocks and dissolves unstable rock minerals, such as olivine, serpentine and piroksin. Mg, Si and Ni will be dissolved and carried in accordance with the flow of groundwater. The iron deposition that becomes a compound with oxide will be accumulated nearby the soil surface, while the magnesium, nickel and silica would remain in the solution and move downwards as long as the supply of water continues penetrating the soil. This series of processes is weathering and leaching process. In the further weathering process, magnesium (Mg), silica (Si), and nickel (Ni) will remain in the solution as long as the water is still acidic. During the oxidation process, it will dissolve Fe until the water reaches acidic condition and the precipitation forming ferrihydrite mineral. Meanwhile, arsenic ions emerge from the dissolution result of olivine and piroksin minerals which are dissolved by rainwater, thus turning into Nickelline mineral (NiAs).

1. The constituent ultramafic rocks type in the research sites, i.e. peridotite, composed of minerals, such as 15%olivine, 25%piroksin, 5% plagioclase, 10%opaque minerals, 35% basic mass and alteration minerals, i.e. serpentine. Metal minerals are also found in the form of Nikellin (NiAs) and Chromium (Cr).
2. The concentration of Arsenic, Cadmium and Chromium Metal Ion contained in the river water of the research sites has exceeded the stipulated threshold according to the Law.
3. A correlation or the relationship is presence between metallic minerals in ultramafic rocks, i.e. peridotite with metal ion concentration in the river.

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