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Study on the Residue Resulted from the Metallic Minerals separations to the Coastal Iron-sand of Yogyakarta Indonesia

Mohammad Nurcholis[1] and Djoko Mulyanto[2]

[1]Study Program of Soil Science, Universitas Pembangunan Nasional "Veteran" Yogyakarta. Jl. SWK (104) Lingkar utara Condongcatur Yogyakarta. 55283. Indoesia.
[1]Email: nurcholis@upnyk.ac.id
[1]Orcid: 0000-0003-0084-7941

[2]Study Program of Soil Science, UPN "Veteran" Yogyakarta. Jl. SWK (104) Lingkar utara Condongcatur Yogyakarta. 55283. Indoesia.

Abstract

South beach of Kulon Progo Regency, Yogyakarta is a boundary on the south side bordered by the Indian Ocean. The sand material of this beach is containing a high value of metal minerals, so that it has a potential to be exploited. Local communities had been managing the land with continuous effort to convert the sandy soil that was extremely low nutrient availability to be the productive farming land. The aimed of the study was to examine the characteristics of minerals and chemistry of the residue produced as a fine-sized material, light metal and also the mineral which may degrades the land and air quality. Analysis of fertility from the residue consist of pH, cation exchange capacity (CEC), and the bases (Ca^{2+}, Mg^{2+}, K^+, Na^+) were extracted using NH_4OAc. Elements analysis of materials was done by neutron activation analysis (NAA). The results of the present study showed that: 1) An increasing of concentration of heavy metal elements namely Ce and Cr on the residue. 2) There were iron minerals (ilmenite, magnetite), silica (crystobalite) and vanadinite potentially degrade the quality of air and soil environment. 3) The processing of iron-sand increase the concentration of minerals as a source of nutrients, namely: feldspar, olivine, augite and amphibole. 4) The residue produced from iron-sand processing can provide the elements of Ca, Mg, K, Na and P required by plants.

Keywords: iron-sand, metal minerals, the residue

INTRODUCTION

South beach of Kulon Progo Regency, Yogyakarta is a boundary on the south side bordered by the Indian Ocean. This area also has a sand dune and is a barrier to people living on the south coast [1](Prastistho dan Nurcholis, 2000). The results of the research that was done by[2] Sukirno (2008) showed that the soil in the sand beach in Kulonprogo have a sand content of 95.9%, silt of 2.3% and clay of 1.8%, a soil density of 3.25 kg/dm^3, besides the temperature air and surface soil is very high. [3]Katim et al, (1994) reported that iron-sand on the beach south of Yogyakarta derived from sand material that is andesitic Merapi volcano through a river that deposited on the beach with ocean waves and the activity of monsoon. Materials sand on the south coast region Kulonprogo regency also have the content of other metallic minerals are high, and these materials also have the potential to be exploited.

Minerals of these metals have high economic value and can support development. Chemical properties of sandy soil is very poor in terms of low levels of elements N, P and K, organic matter, cation exchange capacity values [4](Wada, 2005). But the sandy soil is more easily repaired even if the soil has a low fertility level. Farmer communities in coastal areas with a patiently effort to manage the sandy soil that very poor nutrients but has good physical properties and excellent climate beaches is promising for agriculture. Research in China showed that banana plant that require high availabilities in water and nutrient can be cultivated in the sandy soils [5](Zhao et al., 2000).

In the study site, there will be planned mining and processing of iron-sand located on beach sand, and it includes land along 20 km, 2 km wide with a depth of 3 m. The residue generated from the mining process will be returned to the process of reclamation and later the land will be used as agriculture again. The areas of land that will be to be mined include land already cultivated as farmland. There is a difference of thinking between the policy makers with the farmers who have developed this land as farmland, and now it becomes a big problem.

In the plan the utilization of mineral deposits, NAP (2002)[6] provides guidance in terms of: (1) handling of the quality of groundwater and surface water, (2) harmful elements contained in minerals, the residue and soils, (3) the existence and location of community vulnerable to contamination, (4) the impact of climate on mining operations, including rainfall and wind, and (5) socio-economic and cultural issues and sustainable development. Further in terms of coastal protection and restoration, NRC [7](2009) drafted by taking into account the complex interactions of the condition of beaches, rivers, coastal embankment, raising sea levels and climate change in the future.

The residue generated from processing to extract the minerals metals greatly needs to be studied in detail in terms of physical, chemical and mineralogical. This information will be useful as a material consideration in the preparation of the EIA for the mild nature of the residue, potentially pollution (soil and air), wind direction from the sea towards to the settlements and agricultural land, as well as post-mining reclamation plan with the agricultural food commodities.

Iron-sand in Kulonprogo coastal land, with a high density, contains metallic minerals: magnetite (Fe_3O_4) hematite (Fe_2O_3), ilmenite ($FeTiO_3$), vanadinite {$Pb_5(VO_4)_3Cl$}, zircon ($ZrSiO_4$), titanite (TiO_2), rutile and quartz. Agro-ecosystem condition in this coastal region is very supportive of shallow ground water sources and abundant sunshine. By doing soil amelioration and vessel-connected irrigation system, as the findings of the local community, it was able to convert natural sand-dune land to be productive horticultural farm. By an area of 2000 m2 farmers can get revenue of 15 million rupiahs in one-time harvest (personal communication, 2010). This kind of farming had been already done more than 25 years ago. Ameliorant materials of clay and organic fertilizers were given periodically by them, so that the content of the ameliorant had been risen cumulatively. The environmental benefits derived from this farm are the decrease in air temperature near surface soil and increasing air quality. It is because that the bare sand beach is directly got the heat energy from sunlight. While the croping area the sand surface is protected by crops.

This study was aimed to examine the residue produced as fine-sized materials, light metals and mineral content that can degrade the quality of land and air. In addition, metal elements in the minerals remaining in the residue are potentially available and can be absorbed by plants that cultivated. So that the reclamation process that directly used for agricultural commodity or animal feed crops at risk of metal contamination.

MATERIALS AND METHODS

In conducting this study it was colected samples of sand material from beach of Kulonprogo. To find out the variation of natural processes that sort out metallic minerals, it was carried 10 sampling locations distributed from the east (near the mouth of the River Progo) up to 20 km to the west, as planned mined area. There were10 samples collected along the beach from east to west with a width of 1 km. sampling was handled using a soil auger as deep as 1 m. the collected cores of sand from a depth of 0-1 m were then mixed for materials analysis.

Impurities materials of the sand samples in the form of root grass, a pumice stone or other materials were then separated by a sieve. The result was then crushed by putting into the ball mill. Then the fine materials resulting from crushing was screened with 100 mesh sieve size. The metallic minerals were then extracted from these samples by using a magnetic drum that had a 1200 gauss magnetic intensity. All materials that could be attracted to the magnet were then picked up and delivered 500 gauss magnetic drum. The materials that could not be attracted by the magnetic field were as the residue, and they were probably containing minerals of quartz, rutile, vanadinite, etc. Vanadinite minerals were then separated by using sluice box, and the separation of these minerals were based on the density differences among minerals.

In this study the chemical and mineralogical analyzes on the residue were conducted with the following stages: (1) determination of mineral content of the types that can be extracted and that left in the residue, and (2) determining the level of fertility of the residue. The results then could be used in reclamation process on the post-mining land.

The residual materials from metal extraction process were analyzed using X-ray fluorescence (XRF) to determine the elements detected in these materials. Then the data were analyzed for similarity indices in ordered to group samples with had similarity. Based on the similarity of the sample, it was established 4 samples representing each group for further analysis, ie: 1A, 4A, 2B and 5B.

Fertility analysis of the residue consisted of pH, cation exchange capacity (CEC), and the exchangeable bases of Ca^{2+}, Mg^{2+}, K^+, Na^+, that were done using 1M NH_4OAc pH 7 extraction. Chemical analysis of the residue material was done using neutron activation analysis (NAA), with the principle that the elements of the material are activated to become radioactive. According to the difference of a half-life of each element, the kind of elements in the material is able to be determined, and also a type of elements contained in the material can be determined in one-time analysis.

The fractions of sand and silt-clay of the residue were separated by the fractionation method after the organic matter that contained in the residue was oxydized using hydrogen peroxide (H_2O_2). Separation of fractions sand, silt and clay in the suspension was conducted according to the Stokes law, and collection of the silt-clay fraction was performed using a siphon [8]. Minerals in the fractions of sand and silt-clay were determined using X-ray diffractometer (XRD).

RESULT AND DISCUSSION

A. Mineralogical Characteristics of the Residue

Studied the residue were the result of the sequential extraction processes that were the separation of iron minerals and mineral vanadinite minerals. The residue had finer in size than that the original sand because the extraction processes were preceded by grinding the sand. The identification of minerals contained in these materials was done with separation the coarse fraction with a size of 0.075 to 2 mm and fine fraction with of <0.05 mm. The separation was expected to provide an understanding of minerals that were easily blown by the wind (dust-clay) and the materials that difficult one. Both groups of this fraction were then analyzed by XRD mineralogy.

The determination of mineral types according to the diffraction peaks for the types of mineral that is commonly identified. Based on the results of XRD analysis of the minerals were detected in the fine fraction materials, there were found metallic and nonmetallic minerals. Minerals were detected in samples 1A (Figure 1) were: amphiboles (8.42 Å), feldspar (3.20 Å), olivine (2.82 Å) and magnetite (2.51 Å). Minerals were detected in samples 4A (Figure 2) were: amphiboles (8.17 Å), goetite (6.11 Å), Margarite (4.43 Å), crystobalite (4.02 Å) feldspar (3.20 Å), ilmenite (2.79 Å) and magnetite (2.50 Å). Minerals were detected in sample 3 (Figure 3) were: manganite (4.43 Å) and feldspar (3.20 Å). Minerals were detected in the sample 5B (Figure 1) were: amphiboles (8.23 Å), feldspar (3.20 Å), and magnetite (2.51 Å).

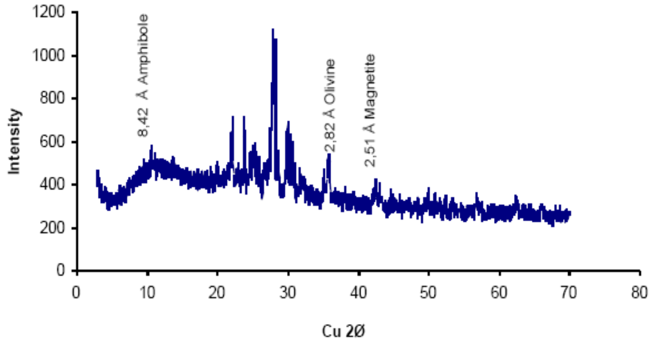


Figure 1: XRD pattern of the fine fractions in the residue of the 1A sample

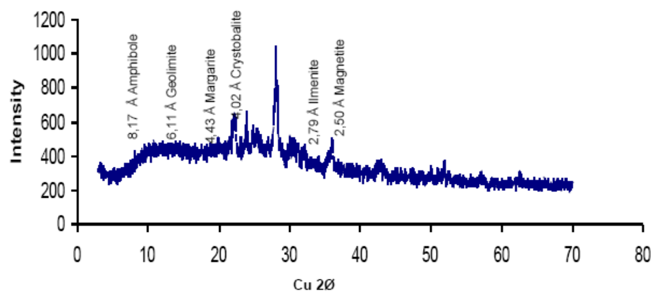


Figure 2: XRD pattern of the fine fractions in the residue of the 4A sample

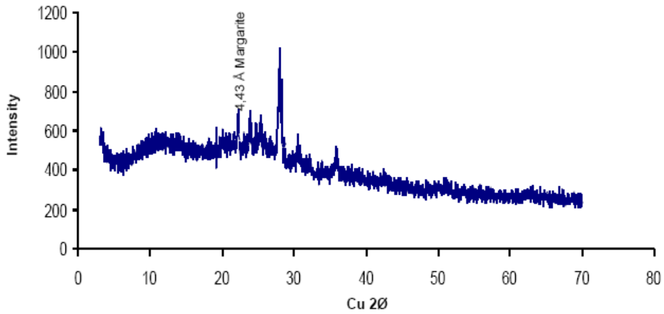


Figure 3: XRD pattern of the fine fractions in the residue of the 3B sample

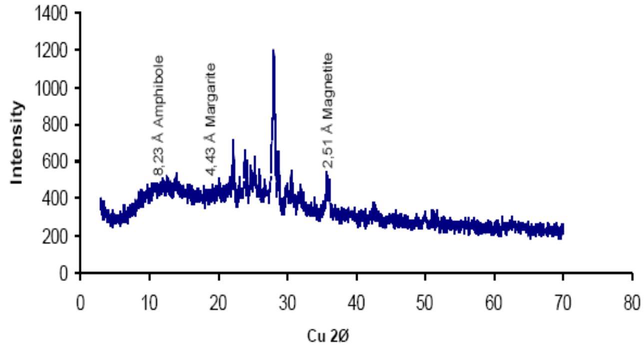


Figure 4: XRD pattern of the fine fractions in the residue of the 5B sample

The increase in sensitivity to magnetic fields of iron minerals in a mineral that has been decaying had been reviewed [9]. There was a positive relationship between the ratio of Fe_2O_3/Al_2O_3, as the value associated with the degree of weathering, to the sensitivity of the magnetic field, however the value of Fe_2O_3 alone did not correlate with sensitivity to magnetic fields. Thus the weathering process causes the conversion of the original Fe_2O_3 less sensitive to the magnetic field becomes more sensitive to magnetic fields.

Metallic minerals that present in the iron-sand in the beach area Kulonprogo consists of magnetite (Fe_3O_4) hematite (Fe_2O_3), ilmenite ($FeTiO_3$), vanadinite ($Pb_5(VO_4)_3Cl$), zircon ($ZrSiO_4$), titanite (TiO_2), rutile and quartz. Environment problem will be able to arise if these minerals are suspended in the atmosphere that cause the air is contaminated by metal minerals. In addition that in one mineral can contain other elements as a result of isomorphic substitution. Paper [10] reported that zircon from magmatic and metamorphic Jianyang region, north of Fujian China has a content element Hf with ratio of ZrO_2/HfO_2 35 to 65. It was reported three series of vanadinite based on the content of CuO and ZnO, namely descloizite, cuprian descloizite and mottramite, which are distinguished based on the analysis using the IR-spectrophotometer [11]. In the mineral titanite reported by [12], the elements Al, Fe, Si, Ca and F. It was also reported

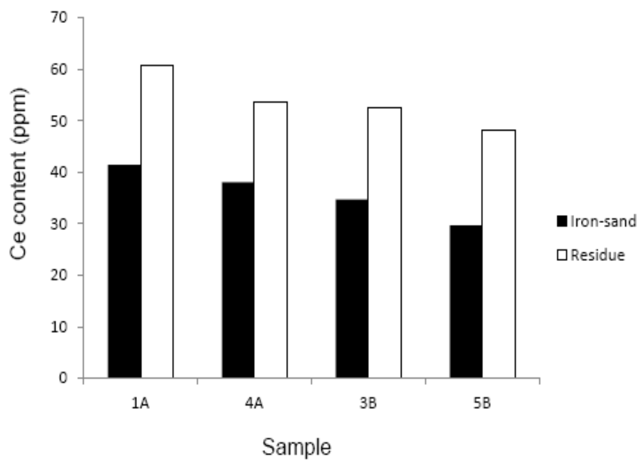
[13] that the existence of elements of V, Ba, Sr, Cu, Zn, Cr and Co in manganese oxide mineral from several locations in Java. TiO_2 can form various types of minerals, among which are rutile, anatase, brookite and TiO_2 (B) [14]. The quartz and feldspar are the primary mineral in the sand and dust fraction in the sediment material from the Methow River, reflecting the soil in the area developed from granite and schist gneiss [15]. The dominant component of the clay fraction includes gibbsite, quartz and muscovite. Minerals such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and galena (PbS) is not detected, whereas elements such as Zn, Cu, and Pb were detected using ICP-AES, and therefore must be as cations that are absorbed by blankets (coatings) on the surface of other primary minerals.

B. Chemical characteristic of the tailing

1. Identified Elements

There was a specific distribution pattern of concentration of certain elements with a function of distance from the mouth of the River Progo to westward. Besides, for certain elements showed a very different in concentration of elements in the residue. There are clear patterns in selected soil samples (with a similarity index) elements Ce and Cr in particular the decline in the function of the distance from the coast and Progo River estuaries. Increases in the two elements (Ce and Cr) in the residue were found in this study (Figure 5).

Measurement of Ce in the iron sand and in the tailings resulted in range of 25-51 ppm and 48-60 ppm, respectively. According to the Figure 5, it can be said that the Ce element in the tailings was roughly higher 35 % compared with in the iron sand. While Cr content in the iron and in the tailings was in the range of 15-65 ppm, and 38-77 ppm, respectively. Figure 5 shows that Cr content is higher in the tailings than in the iron sand at four sites from five sites of research area.



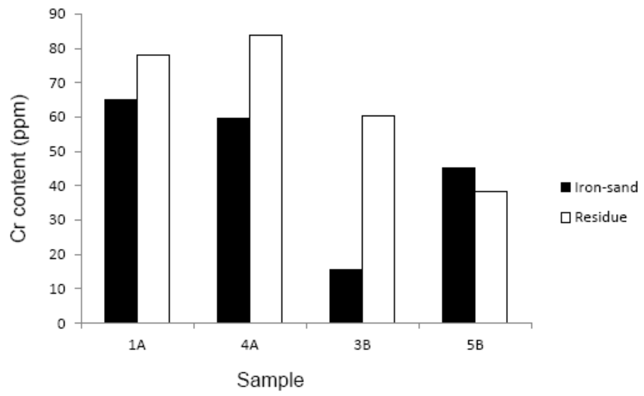


Figure 5: Comparison between Ce and Cr in the iron sand and the tailings

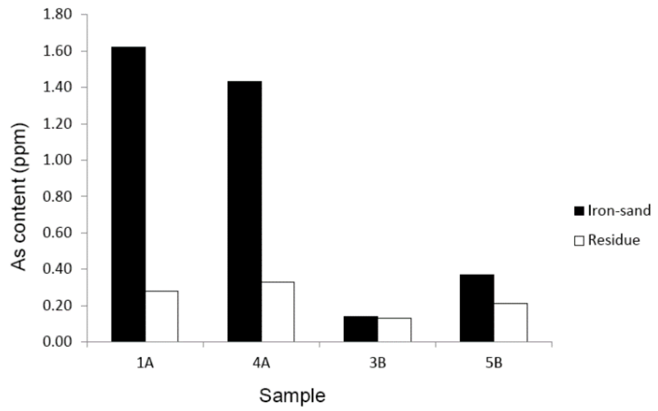


Figure 6: As content in the iron-sand and the residue

The increase in these two elements in the tailings for their decision-metallic minerals, especially Fe and Ti. And also suggests that these two elements do not form compounds with metallic minerals, especially magnetite, hematite, ilmenite and vanadinite. Cr concentration increases by 400% in the tailings at the site 3B, allegedly due to the concentration of iron and vanadinite in these locations is very high. Ce concentration in the tailings above average crust (46 ppm). While the concentration of Cr in rhyolitic rock ± 10 ppm, 130 ppm in mafic rocks, sedimentary rock shale while at 56 ppm. So that the Cr concentration analysis results were allegedly the same relative to the content in intermediate rocks. This is in accordance with the material of the trim that is andesitic.

The results of the study showed that there were increasing in the contents of Ce and Cr in the residue compared to the original iron-sand. Increase in both Cr and Ce elements in the residues due to the separations of metallic minerals, especially iron (Fe) and titan (Ti) elements. Also it is thought that they are not commonly detected in metallic minerals of magnetite, hematite, ilmenite and vanadinite. Cr concentration increased by 400% in the residue on the location 3B presumably caused by the concentration of iron-sand and vanadinite in these locations is very high. Ce concentration in the residues was above the average crust of the earth (46 ppm). While the Cr concentration in rhyolitic rocks ± 10 ppm, 130 ppm in mafic rocks, whereas 56 ppm in shale rock. So that the concentration of Cr was allegedly the result of analysis is relatively the same as the content of the intermediate rocks. This was in accordance with the source of materials of which derived from andesitic material of Merapi volcano.

The result of As analysis in the iron-sand ranged of 0.14 to 1.92 ppm, while in the residue ranged of 0.13 to 0.33 ppm. The distribution of As in the iron-sand showed a very sharp decline in the function of the distance to the beach. Concentration of As in the residue sharply declined until ± 400%, especially in the locations near the coast. This showed that the elements As much bound to iron minerals and vanadinite. In assessing the environmental pollution should be based not only on the magnitude of decrease in the concentration of the element arsenic in the residue. However, it should be observed also that the decrease in the size of the residue resulting from the extraction process can accelerate the release of these elements, and then can impact on environmental quality.

In general there was an increase in K element in the residue compared to the original iron sand. According to the agricultural aspect, it can be considered as an improvement of soil fertility. Increase in K elements in the residue showed that the element was not found in many compounds iron oxides and vanadinite. The K is in the feldspar minerals with the general formula or $xAl(Al,Si)Si_3O_8$, while x can be one or more elements, such as K, Ca and Na.

Sodium was also an increase in the average residue of 1.45% to 1.72%, or 19%. The small increase in concentration of Na in the residue shows that the Na is also as major element of mafic minerals, thus it is considered that partly Na extracted together iron oxide minerals. There was similarity in the content of K and Na elements in the iron sand (Figures 7 and 8). Both elements are derived from the mineral feldspar (K, Na) (Al, Si) $AlSi_3O_8$.

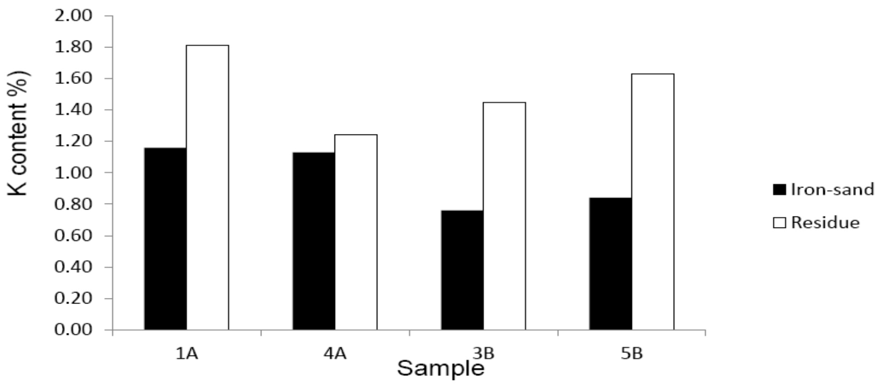


Figure 7: Comparison between K content in the iron sand and in the residue

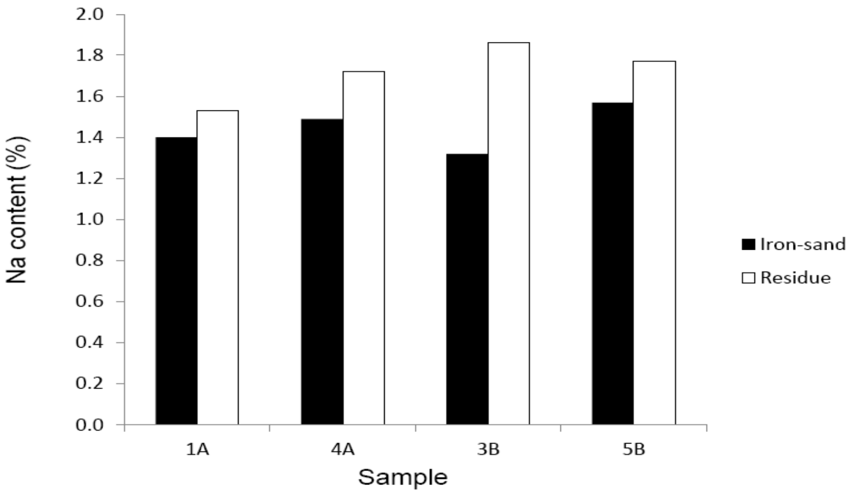


Figure 8: Comparison between Na content in the iron sand and in the residue

2. Fertility of the residue

Table 1 shows that the pH(H_2O) value of the residue as actual acidity was in the range of 7.0 up to 7.4, and the potential acidity or pH(KCl) was in 5.9 to 6.2. Accordingly it can be stated that the nature of the reaction of the residue was neutral so it is favourable for the ecology of vegetable growth. The results of the analysis of available P concentration of the residue showed in variation of 4 ppm to 52 ppm. Phosphorus might be naturally available comes from the mineral apatite minerals. In general, apatite minerals have a chemical formula of $A_5(BO_4)_3(OH,F,Cl)$. Where A is the kinds of cation that can be Calcium (Ca), barium (Ba), sodium Na), lead (Pb), strontium (Sr), lanthanum (La) and or cerium (Ce). While B is kind of cation such as phosphorus (P), vanadium (V) or arsenic (As). Carbonate anion group, CO_3, and a group of silicate anions, SiO_4, might substitute BO_4 groups. Based on the diversity of available P, it can be possible apatite mineral content varying or different kinds of B cation.

Table 1: Chemical analysis of the residue form iron sand extraction

Sample code	pH (1:2.5)		P	Extracted by NH_4 Acetate 1 N, pH 7						
	H_2O	KCl	(Olsen)	Ca	Mg	K	Na	∑	CEC	Base sat.
			ppm	cmol(+).kg^{-1}						%
T1A	7,4	6,2	4	0,76	0,32	0,14	0,07	1,29	1,10	>100
T4A	7,2	6,2	52	0,85	0,31	0,14	0,07	1,37	1,24	>100
T3B	7,0	5,9	17	2,78	0,64	0,17	0,24	3,83	3,64	>100
T5B	7,3	6,1	10	1,53	0,57	0,17	0,13	2,40	2,36	>100

According to the result of the residual materials also shows that the content base cations of Ca, Mg, K and Na at points close to the beach line less is than that in the point distant from the beach line. This is related to the high mineral iron oxides which have a high density so low mobility that causes sortation of this mineral located near the beach ine, while the elements Ca, Mg, K and Na which compose feldspar minerals that is relatively low density that these were sorted far from beach line. This sorting pattern contrasts with the results of the elemental analysis Fe either through X-ray fluorescence and neutron activation analysis (NAA), which indicates the value decreases from the beach. So that the phenomenon of sorting elements strongly associated with a specific gravity of mineral.

C. Potential impact of the residues

Environmental pollutant that is now the subject of urgent discussion is the heavy metals because it is dangerous for living. This is caused by the nature of the heavy metal elements that might be accumulated in water and or soil. The presence of elements in soil can be absorbed by plants and then consumed by the organisms, including humans, then these elements can also be accumulated in the human body. In addition, these elements can also be carried by flowing air as wind which is then inhaled by humans, so in through breathing and mouth. There were quite a lot of Ce, Cr and As elements containing in the residue resulting from the present study of metallic mineral extraction process.

The increase of Ce and Cr concentrations in the residue comparing these in the original sand by ± 35% and 44% respectively, indeed it needs to be addressed. This is because in addition to the increased number of finer size also makes it easier to escape from minerals. Very interesting is precisely the decrease concentrations of arsenic in the residue, i.e., ± 78%, even the residue of iron sand near the beach, a decrease in concentration can reach 400%. From the aspect of the concentration of the residue will greatly benefit the environment, but still needs to be examined because the size is more subtle.

In addition to that the element content in the residue increased in comparison with the material content of the sand before it is extracted. With this need to be taken into consideration if then carried out mining activities and processing, which in this case is taken of iron and vanadinite minerals then the residue generated need to be processed further, ie extracting other elements so that the residue that is produced is not containing elements that endanger the lives human.

Cultivation of food crops on land with the residue materials have potential absorption elements such as Ce, Cr and As into a plant, which then when consumed by humans can potentially interfere with human health. Alternative solutions that can be do by cultivating non-food crops (non-edible), so taken or consumed instead of as food.

D. Fertility potential of the residue

Based on the results of the analysis of the chemical properties of the residue indicates the status of the nutrient availabilities particularly for exchangeable bases (Ca, Mg, K, and Na) were very low (Table 1). Similarly, of the cation exchange capacity (CEC) value of the residue was also very low (1.10 to 2.36 cmol(+). kg^{-1}). Status of the residue of actual fertility is low, but the results of the total analysis of K and Na using neutron activation analysis showed excellent value. According to the result it can be stated that the residue has a high potential fertility status. To improve the actual fertility, it is needed appropriate techniques to induce availabilities of nutrients in the residue, such as organic substances application. In order residue has ability to save and exchange of nutrients for plants, it is also needed fine materials with high content of negative charge, like smectite or vermiculite clay minerals, as ameliorant. Addition of fine materials to the residue also may result aggregate formation that it may increase the resistance to wind erosion.

CONCLUSION

Based on the results of the analysis of mineralogical and chemical characteristics of the iron ore processing residue resulted in iron-sand extraction from the sand beach in Kulon Progo Regency, which have an influence on the biophysical environment are: 1) An increase in the concentration of heavy metal elements of Ce and Cr in the residue. 2) There are iron minerals (ilmenite, magnetite), silica (crystobalite) and vanadinite might potentially degrade the quality of the air and the soil environment. 3) Sand iron containing Cu and Pb elements that exceed the average of the content contained in most rocks and potential increases both elements on the residue. 4) The results of the processing of iron sand can increase the concentration of minerals as a source of nutrients, namely: feldspar, olivine, augite and amphibole. 5) The residue resulting from the processing of iron sand can provide the elements Ca, Mg, K, Na and P are needed by plants.

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