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REE-Bearing Minerals in Tin Waste Dumps of Singkep Island: Geochemical Identification and Recovery

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Abstract - Instead of environmental hazard, tailing might contain resources which could be reworked with the development of mining and separation technologies. Tailing dumps and waste ponds which associated with the long period of tin mining are easily found in Singkep Island. The waste should be processed to recover and purify precious metals within, and to reduce environmental degradation. REE-bearing minerals identification in tin tailing based on trace and rare earth element abundances is the aim of this study. Concise mineral beneficiation is illustrated for any further re-work strategy. The tailings collected from four locations in Singkep were analyzed for their trace and rare earth element compositions using ICP-MS at The Centre for Geological Survey. REE content in concentrates was upgraded at the range of 9 to 94 folds of the corresponding wastes. Monazite-(Ce), xenotime, and zircon are the REE-bearing minerals of the studied samples according to the elemental composition. Gravity, flotation, magnetic, and electrostatic methods would be applicable to separate the REE-bearing minerals from the tailing.

Keywords: REE-bearing minerals, tailing, geochemistry identification, recovery

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Introduction

Mining works are conducted to separate special geological materials from the earth. Such activities also produce tailing as the waste of extraction process comprising the mixture of ore, sand, and initial minerals in separating valuable metal from a particular ore (Zulfahmi *et al*., 2012; Irzon *et al*., 2014; Irzon *et al*., 2020a). Several environmental problems might come from the exploitation waste. Large area of floodplain which underwent extensive degradation in the quality, diversity, vegetation, and wildlife is filled with solid disposal material (Romero *et al*., 2010; Andrews *et al*., 2013; Eqani *et al*., 2016; Irzon *et al*., 2018). Radionuclides and hazardous substances in remained exposed tailing could be transported to vegetation via root uptake or win, water sources by flood wash-down, and residential homes when the tailing applied as building materials (Romero *et al*., 2010; Andrews *et al*., 2013; Olise *et al*., 2014; Kumari *et al*., 2015; Irzon *et al*., 2018). Silicosis, nasal irritation, skin illness, intractable vomiting, diabetes, and gastrointestinal problem are some disease which might be happened because of mine waste toxicity (Mudhoo *et al*., 2011; Andrews *et al*., 2013; Hassan *et al*., 2014; Eqani *et al*., 2016).

Although tailing is widely thought as harmful, toxic, and unfriendly material for the environment, the amount of potential resources from the waste draws attention, especially in the last two decades. The abandoned materials might be reworked when mining technology and market demand makes their extraction worthwhile again (Andrews *et al*., 2013; Edraki *et al*., 2014; Gutiérrez-Gutiérrez *et al*., 2015). Froth Flotation, extraction, and magnetic separation techniques were adapted to beneficiate tin, iron minerals, and cassiterite from tin mining wastes (Zhou *et al*., 2014; Su *et al*., 2017; Abaka-Wood *et al*., 2019). Scandium recovery from slag, tailing, and waste liquor using hydro- and pyro-metallurgical processes was developed because of the growth of the value and market demand (Wang *et al*., 2011). New inventions helped tin production from renewable source to reach almost 30% of the global tin consumption (Su *et al*., 2017).

Tin mining has been initiated since the Dutch colonial period in the tin islands located on the east of Sumatra, namely Karimun, Kundur, Singkep, Bangka, and Belitung. After the independence proclamation, metal exploitation is mainly worked by PT Timah Tbk. to give a big impact on the local and national economy. Because of a long time of mining activity, tailing dumps and waste ponds are easily found in many locations in Singkep Island. Irzon *et al*. (2014) investigation focused on the tin tailing REE compositional value from three sites in Singkep, whilst Irzon *et al*. (2018) summarized the concentration tendency of five heavy metals and the pollution index. Applying SEM/EDAX, Hamzah *et al*. (2018) revealed REE-bearing monazite occurrence in waste sites at Kuala Raya.

Geochemistry character which refers to the chemical composition of geological materials is a tool for predicting the mineral composition. Mining wastes should be processed to recover and purify precious metals within and reduce some environmental degradation. Tin tailing beneficiation is attractive as the material is located on the surface with a soft texture and a large surface area. Separation and purification methods are needed to gain high purity which parallels the metal market price. The price of rare-earth metals and some related material is listed in Table 1. A complete

Table 1. Price of Rare-Earth Metals and Zircon

Metals	Description	Market value (metric ton/US dollars)*
Zr	Zircon sand Indonesia ($ZrHfO_2$ 66%)	1,400
Ce	Cerium metal (99%)	3,943
Dy	Dysprosium metal (99.5%)	335,000
Tb	Terbium metal (99.9%)	711,270
Eu	Europium metal (99.5%)	288,000
Gd	Gadolinium oxide (99.5%)	21,549
Ho	Holmium oxide (99.5%)	48,590
La	Lanthanum metal (99%)	4,507
Nd	Neodymium metal (99%)	50,845
Sm	Samarium metal (99.5%)	13,240
Sc	Scandium metal (99.99%)	3,070
Y	Yttrium metal (99.9%)	30,700
Pr	Praseodymium metal (99.5%)	92,000

Open market value for Th and U is not available, buyers and sellers should negotiate in private.
*Source Metal Prices.com (2020)

analysis would encourage re-exploitation works of dumpsites (Edraki *et al*., 2014; Kumari *et al*., 2015). The purpose of this paper is to identify REE-bearing minerals in four tailing dumps from Singkep based on the trace and rare earth element compositions. A concise description of mineral beneficiations is also given as an option in any further re-work strategy.

Geological Setting

Singkep Island is situated in Lingga Regency of Kepulauan Riau Province. The climate of the island is tropical with dry and rainy seasons as located near the equator. The average temperature in the studied area is 28°C and the range of yearly rainfall is 1,000−3,000 mm. According to geological perspective, Kepulauan Riau Province is divided by an imaginary line called Bentong Raub Suture which extends to Malaysia. Granite rocks at the east of the suture are mostly classified as I-type, while in the west as S-type (Cobbing, 2005; Irzon, 2015; Irzon *et al*., 2016; Mustafa dan Usman, 2016; Irzon, 2017; Irzon *et al*., 2020[b]). The S-type granites in Bangka, Belitung, Kundur, Karimun, and Singkep are associated with tin mineralization which well-known as the tin islands. Industrial tin mining in Singkep started in the colonial period by *NV Singkep Tin Exploitatie Maatschappij* which was nationalized and merged with other three Dutch mining companies into PT Timah Tbk.

Based on the Geological Map of the Dabo Quadrangle (Sutisna *et al*., 1994), the studied area is generally constructed of several rock units from the older to the younger, namely Duabelas Bukit Quarzite, Persing Complex, Muncung Granite, Tanjungbuku Granite, Alluvium, and Swamp Deposit. Most of the land is occupied by Persing Complex with the alternation of phyllite, slate, and graphitic schist with quartz veins, whilst Duabelas Bukit Quarzite is located in some areas at the north. Both of the metamorphic units were emplaced during Carboniferous to Permian. The Triassic S-type Muncung Granite can be found in the northeast while the Jurassic I-type Tanjung Buku on the southwest tip of Singkep. Ferroan, strong peraluminous, and alkali-calcic nature of Muncung Granite were revealed in the previous study (Irzon *et al*., 2015) using geochemistry interpretation. Most of the coastal region of the island is occupied by the Holocene Alluvium and Swamp Deposit. The geological map of the studied location is shown in Figure 1.

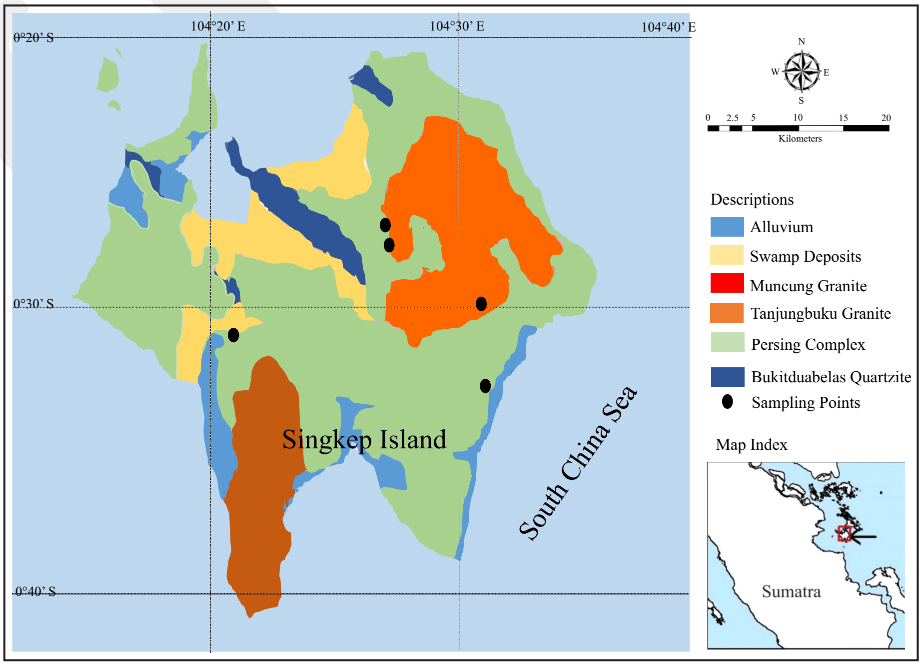

Figure 1. Location map showing rock units in Singkep Island and the sampling points (modified from Sutisna *et al*., 1994).

Analytical Method

Identifying tin waste sites are simple as generally composed of quartz, Ca-K- and Na-feldspar, clay minerals, Ti-oxides, and carbonates in a large area (Figure 2a). Metal composition in the waste correlated negatively to the quartz abundance (Irzon *et al*., 2018). The studied tailings were taken not more than 50 cm below the surface at four locations. TRE 51 I is dominantly composed of reddish clay with a small amount of quartz sand and dark granules grabbed from Bakong Village as newly dumped tailing of recent re-mining activity. TRE 59 with no re-mining activity is located about 1 km southwest of TRE 51 I. TRE 59 is a mixture of quartz sand and reddish clay with minimum dark material.

A large amount of white-yellowish fine sand was found in TRE 65 A which was situated close to a three-way junction in Marok Tua. TRE 76 was taken near the eastern shore of Singkep Island in Batu Berdaun Village. Local inhabitants of Batu Berdaun conducted simple re-mining works as in Bakong Village for secondary tin exploitation (Figure 2b). After sieving, the wastes from four locations were then separated into two groups: the tailings and concentrates which were the -80-mesh fraction of the selected tailings. The content of heavy metals Cr, Pb, As, Ba, and V from TRE 51 I, TRE 59, TRE 65 A, and TRE 76 were discussed by Irzon *et al.* (2018) on an environmental study in Singkep. As tin mineralization in Singkep closely associated with the S-type intrusion, a fresh rock from Batu Kacang of Muncung Granite is also analyzed for comparison.

Figure 2. Some field conditions of the studied area: a) A large area of tin mining disposal near Bakong Village; and b) Re-mining works by local inhabitant in Batu Berdaun.

Studied samples were sent to Geology Laboratory of the Indonesia Centre for Geological Survey in Bandung for Thermo X-Series Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) measurements. The equipment was selected because of its good sensitivity on measuring trace and rare earth elements (Andrews *et al*., 2013; Irzon *et al*., 2014; Eqani *et al*., 2016; Irzon *et al*., 2018). The hard rock sample was washed to remove impurities, whilst the tailings and concentrates were directly dried outdoor for a day in minimum. The samples were then crushed and milled to gain the fraction of <200 mesh. All laboratory equipment had been previously washed using 2% HNO_3 and rinsed with de-ionized water before used. Nitric acid (HNO_3), Hydrofluoric acid (HF), and perchloric acid ($HClO_4$) were selected for acid destruction. ICP-MS was set up according to the recommended parameters of the previous study (Irzon *et al*., 2016).

Results and Discussion

Measurement Results

The five most abundant elements in granite sample are Rb, Mn, Cr, Li, and Zr of 346 ppm, 206 ppm, 191 ppm, 102 ppm, and 58 ppm, respectively. Although Zr, Cr, Mn, and Rb are dominant in the tailing samples with mean values of 374 ppm, 165 ppm, 129 ppm, and 112 ppm, respectively, no element of this group detected above 1,000 ppm. The average concentrations of Lu, Ho, Tb, and Eu in tailings are low <1 ppm. In contrast, Ce, Zr, and Mn are sufficient in the concentrates exceeding 1,000 ppm. Moreover, seven other measured elements, namely La, Nd, Y, Th, Pb, Pr, and Sm are found in large values of >100 ppm. Li, Be, Ga, Rb, Sr, Cr, and Cs are more effusive in granite than both sieved and unsieved wastes. Even though As concentration in granite is higher than tailings, it is relatively at the same value of the concentrates. The other trace elements are much more enriched in the sieved tailings.

Sc and Y are included in the REE group in this study because of their general occurrence in the similar ore deposits and identical chemical property (Gutiérrez-Gutiérrez *et al*., 2015; Kumari *et al*., 2015). REE content in granite of 194 ppm decreased slightly in the tailings of 172 ppm on the average, but largely raised to an average of 4,212 ppm after sieving. The three most abundant REEs in hard rock, tailings, and concentrates are Ce, La, and Nd. All of REEs are more abundant in concentrates than both granite and tailings. Simple sieving work increased the REE content in concentrates at the range of 9 to 94 folds of the corresponding wastes. The measurement result in this study is given in Table 2.

Discussion

REE-bearing Mineral Identification

Lithium forms a minor part of igneous rocks, and appears in the highest composition in granites (Tadesse *et al*., 2019). Together with K and Na, Li is the elements that can float on the oil and water as the density is <1 g/cm^3 (Taheri *et al*., 2011). Li content in the unsieved tailing samples (average of 34 ppm) is about one third than the fresh rock (the average of 62.70 ppm), and drop to averagely 10.15 ppm of the concentrates. A similar concentration tendency is shown on Beryllium which is the least dense metal after Lithium in this study. These two metals indicate a very strong correlation with the coefficient of 0.94 (Table 3). The very low Li and Be abundances in the sieved samples should because of their low density which makes them float and remain at the top of the filter. Besides, the low Be concentration in tailings is counted as an advantage because of its high carcinogenic nature (Armiento *et al*., 2013).

Vanadium consumption is very high in this decade because of the utility for alloy steel in combination with wolfram, manganese, chromium, boron, and nickel. Despite its high toxicity, a previous study by Irzon *et al*. (2018) explained that the range of vanadium compositions in these tailings is not environmentally dangerous. The V composition in the concentrates is averagely 2.5 fold of granite. Naturally, vanadium concentration in soils and sediment relies on the parent material and V-containing minerals. Moreover, anthropogenic activities such as pesticide, burning of fossil fuels, iron refining, and dyeing release vanadium to the environment (Irzon *et al.*, 2018; Gustafsson, 2019). TRE 65 was attained close to the roads and should be affected by fossil fuel combustion to reflect their elevated vanadium abundance.

The tendency of Rb and Sr contents in mine wastes is rarely discussed. However, their compositions on unaltered igneous rock exhibit their common existence in plagioclase. The lower Rb and Sr values in the wastes in relative to granite depict plagioclase lost after tin extraction from the rock. This fact fits the Europium tendency which is described below. The Rb and Sr show a positive correlation with each other, but portray no distinct correlation to any other measured elements (Table 3).

The better correlation coefficient of Y to heavy-REEs than the light ones (Table 3) amplifies the previous grouping of REE (Koltun and Tharumarajah, 2014). Valuable REE-rich minerals such as monazite, zircon, xenotime, and ilmenite are associated with tin mining wastes (Zulfahmi *et al*., 2012; Olise *et al*., 2014; Kumari *et al*., 2015; Irzon, 2018). The large Ce, La, Nd, and Th compositions indicate monazite abundance in the studied locations, especially

Table 2. Measurement Results of the Studied Samples

	TRE 51 I		TRE 59		TRE 65 A		TRE 76		RGI46
	T	C	T	C	T	C	T	C	G
Trace elements concentration (ppm)									
Li	33.07	5.30	73.18	17.77	7.40	14.65	22.89	14.90	102.76
Be	2.00	1.24	2.07	1.02	0.74	0.96	1.17	1.01	3.10
V	8.18	12.00	8.48	18.91	17.95	47.00	21.52	38.39	12.25
Cr	316.58	20.16	125.84	64.79	132.77	67.43	86.04	57.20	191.21
Mn	245.30	2534.00	51.93	264.60	52.73	1334.55	168.00	1095.00	206.70
Ga	4.73	7.15	9.86	2.33	2.71	4.16	0.76	2.34	6.51
As	68.43	62.30	24.58	23.68	2.76	65.26	19.73	30.11	43.98
Rb	70.38	4.62	335.28	12.23	21.30	4.51	22.42	11.14	346.71
Sr	3.99	5.02	7.47	2.46	5.30	8.50	3.04	8.47	15.95
Zr	825.38	3190.00	95.47	699.02	479.22	1065.12	99.78	2032.80	58.46
Cs	8.89	0.77	20.86	2.33	0.79	0.71	2.33	1.10	26.50
Ba	17.24	238.56	104.88	12.49	24.28	37.12	24.14	16.97	54.28
Pb	71.07	908.70	33.76	24.89	14.69	88.27	6.69	37.09	48.35
Th	70.92	266.28	37.68	132.83	23.12	427.35	2.64	447.93	29.10
U	20.17	91.95	8.94	25.42	8.88	51.69	2.26	72.66	12.87
Rare earth elements concentration (ppm)									
Sc	6.02	12.35	4.03	2.94	2.12	10.46	0.93	9.08	3.28
Y	62.01	682.00	7.36	167.52	13.24	278.16	3.75	240.24	53.82
La	44.55	250.47	23.30	327.24	24.08	1109.40	12.35	1150.32	24.95
Ce	147.32	1120.35	58.21	785.76	48.86	2666.40	27.65	2685.60	37.99
Pr	11.85	109.73	5.87	81.16	5.03	282.92	2.69	277.42	6.74
Nd	43.73	488.30	20.30	304.15	16.58	969.10	9.76	935.66	25.93
Sm	11.87	181.13	4.63	69.68	3.29	238.75	2.06	218.00	6.55
Eu	0.07	0.53	0.10	0.58	0.20	1.05	0.28	1.96	0.18
Gd	9.43	117.60	2.66	45.02	2.37	138.40	1.36	130.30	7.26
Tb	1.44	19.22	0.37	6.92	0.41	18.23	0.20	16.39	1.39
Dy	9.43	130.94	1.90	33.68	2.39	75.25	0.89	66.08	9.77
Ho	2.06	22.60	0.33	6.88	0.57	13.21	0.18	11.31	2.03
Er	6.39	63.07	1.06	17.39	1.70	30.87	0.55	27.13	6.11
Tm	1.33	12.29	0.19	3.10	0.34	5.13	0.11	4.37	0.94
Yb	9.14	81.05	1.28	20.46	2.49	32.14	0.85	29.19	6.33
Lu	1.47	11.07	0.22	2.77	0.47	4.76	0.17	4.78	0.90
∑REE	*300.07*	*2608.32*	*120.43*	*1704.78*	*108.78*	*5585.61*	*59.08*	*5558.50*	*137.08*

T= tailing, C= concentrate, and G= granite

monazite-(Ce). Extremely strong correlations are shown from these elements with coefficients ≥0.95. This conclusion is in line with another tin waste investigation around Kuala Raya at the north of studied locations (Hamzah *et al*., 2018). Xenotime in the selected samples might point out from the high content of Y which reaches 682 ppm of TRE 51 concentrate. Moreover, the strong and very strong positive correlations of Y to U and Th, respectively affirm xenotime existence.

Europium is the most reactive in REE group, because it exists in divalent oxidation state and its behaviour is strongly influenced by plagioclase. Since plagioclase is one of the most minerals to chemical dissolution, Eu is easier to fractionate from other REE during weathering (Alsalam *et al*., 2020). Eu should have been fractionated from lanthanide group during long period of waste dumping on describing its lower correlation coefficient to the other REE elements. An

Table 3. Elements Correlation Coefficient of the Samples from Singkep

	Be	V	Cr	Ga	As	Rb	Sr	Zr	Ba	Sc	Y	La	Ce	Pr
Li	0.94	-0.46	0.46	0.58	0.02	0.97	0.72	-0.56	-0.02	-0.36	-0.45	-0.40	-0.45	-0.44
Be	1.00	-0.57	0.60	0.60	0.28	0.87	0.67	-0.38	0.10	-0.20	-0.29	-0.45	-0.47	-0.46
V		1.00	-0.49	-0.49	0.08	-0.51	0.07	0.22	-0.34	0.41	0.19	0.91	0.87	0.88
Cr			1	0.16	0.23	0.37	0.15	-0.47	-0.36	-0.34	-0.56	-0.47	-0.52	-0.52
Ga				1	0.34	0.71	0.41	0.07	0.65	0.27	0.19	-0.26	-0.21	-0.21
As					1	-0.05	0.17	0.45	0.35	0.71	0.53	0.27	0.34	0.33
Rb						1	0.70	-0.51	0.10	-0.32	-0.42	-0.43	-0.47	-0.46
Sr							1	-0.16	0.02	0.1	-0.08	0.15	0.11	0.13
Zr								1	0.62	0.86	0.93	0.46	0.58	0.55
Ba									1	0.55	0.75	-0.16	-0.02	-0.03
Sc										1	0.86	0.65	0.74	0.73
Y											1	0.39	0.52	0.51
La												1	0.99	0.99
Ce													1	1

Positive correlation

Strong positive correlation

Very strong positive correlation

	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Pb	Th	U
Li	-0.46	-0.50	-0.41	-0.50	-0.51	-0.48	-0.49	-0.47	-0.46	-0.46	-0.48	-0.29	-0.46	-0.47
Be	-0.47	-0.46	-0.46	-0.45	-0.43	-0.35	-0.35	-0.31	-0.30	-0.29	-0.31	-0.10	-0.44	-0.34
V	0.85	0.76	0.81	0.72	0.63	0.37	0.36	0.27	0.19	0.17	0.23	-0.20	0.80	0.40
Cr	-0.56	-0.60	-0.53	-0.61	-0.63	-0.61	-0.60	-0.58	-0.55	-0.55	-0.55	-0.38	-0.51	-0.54
Ga	-0.18	-0.09	-0.35	-0.07	-0.01	0.12	0.11	0.15	0.18	0.18	0.16	0.37	-0.12	0.09
As	0.37	0.45	0.07	0.46	0.50	0.53	0.54	0.54	0.54	0.53	0.54	0.47	0.42	0.50
Rb	-0.48	-0.50	-0.44	-0.50	-0.50	-0.46	-0.46	-0.44	-0.42	-0.42	-0.44	-0.23	-0.47	-0.45
Sr	0.11	0.07	0.11	0.07	0.03	-0.03	-0.04	-0.06	-0.09	-0.10	-0.08	-0.12	0.11	0.01
Zr	0.62	0.75	0.53	0.79	0.84	0.93	0.92	0.94	0.93	0.94	0.96	0.82	0.69	0.96
Ba	0.05	0.24	-0.15	0.29	0.40	0.64	0.63	0.69	0.74	0.74	0.71	0.92	0.11	0.55
Sc	0.78	0.87	0.55	0.89	0.91	0.91	0.90	0.88	0.86	0.85	0.88	0.67	0.83	0.93
Y	0.59	0.74	0.38	0.78	0.86	0.98	0.98	1.00	1.00	1.00	1.00	0.90	0.63	0.92
La	0.97	0.90	0.93	0.88	0.80	0.56	0.56	0.47	0.39	0.38	0.44	-0.02	0.95	0.64
Ce	1.00	0.96	0.92	0.94	0.88	0.69	0.68	0.61	0.53	0.52	0.57	0.14	0.99	0.75
Pr	1.00	0.96	0.92	0.94	0.88	0.69	0.68	0.61	0.53	0.52	0.57	0.14	0.99	0.75
Nd	1.00	0.98	0.90	0.97	0.92	0.74	0.74	0.66	0.59	0.58	0.63	0.21	0.99	0.79
Sm		1.00	0.83	1.00	0.98	0.86	0.86	0.80	0.75	0.74	0.78	0.41	0.98	0.89
Eu			1.00	0.82	0.74	0.54	0.53	0.46	0.38	0.38	0.44	0.00	0.89	0.67
Gd				1.00	0.99	0.89	0.89	0.84	0.78	0.77	0.81	0.46	0.97	0.91
Tb					1.00	0.95	0.94	0.91	0.86	0.86	0.89	0.58	0.93	0.95
Dy						1.00	1.00	0.99	0.98	0.98	0.99	0.81	0.77	0.96
Ho							1.00	0.99	0.98	0.98	0.99	0.80	0.77	0.96
Er								1.00	1.00	0.99	1.00	0.86	0.70	0.95
Tm									1.00	1.00	1.00	0.90	0.64	0.92
Yb										1.00	1.00	0.90	0.63	0.92
Lu											1.00	0.88	0.68	0.95
Pb												1.00	0.27	0.72
Th													1.00	0.84

extensive composition of Zr is identified in this study. Zr content from 58 ppm in granite raises to a mean value of 375 ppm in tailings and reaches >1,300 ppm averagely of sieved wastes. The significant correlation between Zr and HREEs (including Y) in the coefficient range of 0.82 to 0.91 might indicate the occurrence of Zr-bearing silicate minerals (Simandl, 2014; Edahbi *et al.*, 2018). The positive correlation of U and Th to Zr (Table 3) is due to the fact that these elements are incorporated into the zircon crystalline structure (Aral *et al*., 2008).

Possible Advantages of Environmentally Hazardous Material

Severe arsenic pollution was illustrated from mine waste in Singkep (Irzon *et al*., 2018) with the mean concentration of 28.87 ppm and 45.34 ppm in unsieved samples and sieved ones respectively. Pollution is widely known as natural world calamity, especially in areas with high As concentrations in groundwater. However, few attempts were made to solve the arsenic problems. Hassan *et al*. (2014) used the sludge of arsenic and iron to make bricks as a potential substitute for brick clay. In medical aspect, several arsenic derivates are used in the treatment of multiple myeloma and leukemia (Mudhoo *et al*., 2011). The enrichment and distribution of monoclonal antibodies in tumor tissues is drawn based on the half-lives of ^{72}As and ^{74}As.

A large amount of Pb availability in tin and the possibility of being separated through the tin production are the reasons of the considerable Pb concentration in the tailings (Mansor *et al*., 2010; Romero *et al*., 2014). Simple 80 mesh sieving enlarges Pb content to averagely eight folds of the waste. Lead is thought to be environmentally dangerous which its uses in solder had been replaced by other elements and Pb-containing fuel had been banned since 1990 by EPA (Eqani *et al*., 2016). Besides, the prevalence of lead as a heavy element enhances detector sensitivity to hard gamma-radiation and might explain Pb-U strong correlation in this study. The device is then applicable for radiation safety and protection of active nuclear reactors zones (El-Sayed *et al*., 2015).

As discussed above, the content of uranium and thorium corresponds to monazite, xenotime, and zircon existences. Uranium and thorium are sources of radioactive radon gases (Hamzah *et al*., 2018). Thorium can be stored in bones to cause bone cancer many years after the exposure has taken place. Uranium toxicity would lead to memory disorders, insomnia, depression, dizziness and headache, muscle weakness, joint pain, skin inflammations, and disorders of the cardiovascular system (Gudkov *et al*., 2016). In spite of the hazards, these elements are urgent for a nuclear power plant. Thorium, especially Th-232, is a relatively inexpensive material for ore impurities separation (Schaffer, 2013). Moreover, thorium reactors produce substantially less long-lived radioactive waste and fully reducible actinides than uranium ones.

Possible REE Recovery Scheme

Gravity, magnetic, flotation, and electrostatic techniques are developed to separate valuable minerals physically. Free quartz, plagioclase, biotite, and other light mineral gangue separated from monazite, xenotime, and zircon of containing alluvial waste using tetrabromoethane (Specific Gravity= 2.95 g/cm^3) as the heavy liquid (Aral *et al*., 2008; Kim and Jeong, 2019). Flotation part mineral by modifying their surface characters to a hydrophobic or hydrophilic condition, whilst magnetic method separates ferromagnetic and paramagnetic minerals using magnets. At room temperature, xenotime depicts a paramagnetic response, while zircon has a non-paramagnetic one. Moreover, xenotime is more strongly paramagnetic than monazite (Kumari *et al*., 2015; Moghise *et al*., 2016) to denote the possibility for these mineral separation using different magnetic intensities. The combination of froth flotation and magnetic separation is effective for beneficiation of iron oxide-silicate rich tailing (Edraki *et al*., 2014; Abaka-Wood *et al.*, 2019). The more conductive Ti-rich materials were successfully detached from the three REE-bearing minerals using the electrostatic method (Aral *et al*., 2008; Kumari *et al*., 2015; Moghise *et al*., 2016).

REE purification ordinarily utilizes chemical solutions to attain individual compounds as REOs (rare earth oxide). Acid method and caustic soda methods were developed to purify and separate REE from monazite and xenotime (Abdelkader *et al*., 2008; Kumari *et al*., 2015; Pusporini *et al*., 2020). Although acid method is relatively simpler than caustic soda, the latter technique is preferred for tailing in Singkep for a clean result (Abdelkader *et al*., 2008; Pusporini *et al*., 2020). Moreover, trisodium phosphate (Na_3PO_4) which remained in solution after REE precipitation through caustic soda technique is a marketable byproduct (Kumari *et al*., 2015). Ion exchange and solvent extraction methods are available on refining different metals of rare earth group (Koltun and Tharumarajah, 2014; Chelgani *et al*., 2015; Gutiérrez-Gutiérrez *et al*., 2015; Kumari *et al*., 2015). Solvent extraction separates REE ions in aqueous solution using extractant in an organic phase and is environmentally friendly which could purify the Th and U in the waste (Kumari *et al*., 2015). As solvent extraction works best for LREE separation, the technique is more suitable with REE refinery in monazite, whilst ion extraction would be better for xenotime and zircon (Koltun and Tharumarajah, 2014). A simple design that is suitable for REE beneficiation of the studied location is shown Figure 3.

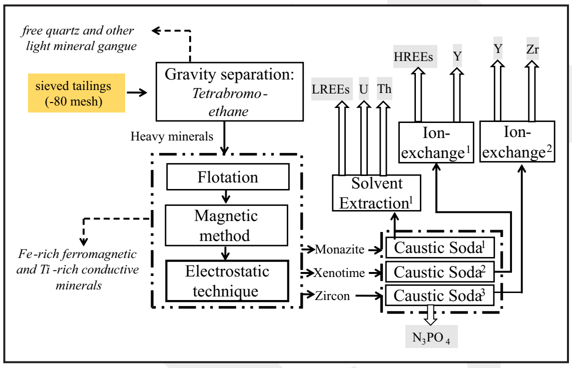

Figure 3. Simple proposed scheme for REE recovery from tin tailing in Singkep Island

Conclusions

Tailing dumps in Singkep are closely correlated with tin mining which had been initiated since the colonial period. The wastes should be processed to reduce environmental hazards and recover available precious material within. Moreover, located on the surface, soft texture, a large surface area, and recent developments in mining technology would simplify the waste re-work process. Eight samples from four locations in Singkep were analyzed using ICP-MS to identify REE-bearing minerals. REE content escalation up to ninety-four folds was simply obtained by passing the tailing through an 80 mesh sieve. The abundances of LREE-Th-U, HREE-Y, and Zr-Y of the samples imply the occurrence of monazite-Ce, xenotime, and zircon, respectively. A beneficiation process consisting of gravity, flotation, magnetic, and electrostatic separations are proposed for REE recovery from the tin waste is Singkep.

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