

Article

Selective Leaching Trace Elements from Bauxite Residue (Red Mud) without and with Adding Solid NH_4Cl Using Microwave Heating

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Abstract: Bauxite residue (red mud), which is an industrial byproduct, contains valuable trace elements. Solid NH_4Cl was used as a chlorinating agent during the microwave heating of red mud to convert trace elements into soluble metal chloride. Red mud was heated using microwave ovens under various conditions (i.e., with the addition of solid NH_4Cl and with a range of microwave output powers and microwave heating times). Leaching tests were then conducted using deionized (DI) water on the microwave-heated red mud to leach trace elements from red mud. V, Cr, and As were selectively leached from the microwave heated red mud slurry (30% water content), whereas Mn, Cu, Co, Ni, Zn, and Pb were selectively leached from the microwave-heated red mud with the addition of solid NH_4Cl . The oxides of V, Cr, and As in red mud could be transformed into metal chlorides by chlorination, which are insoluble in water, or could be easily volatilized when red mud was microwave-heated in the presence of solid NH_4Cl . On the other hand, the oxides of Mn, Cu, Co, Zn, Ni, and Pb in red mud could be heated rapidly by microwave irradiating, resulting in metal chlorides in the presence of solid NH_4Cl . Those metal chlorides are relatively soluble in water, leading to higher leaching efficiency for microwave-heated red mud with the addition of solid NH_4Cl . Experimental results suggest that trace elements from red mud can be selectively leached by microwave heating of red mud without or with the addition of solid NH_4Cl .

Keywords: red mud; trace elements; microwave heating; ammonium chloride; leaching



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1. Introduction

Red mud is an industrial byproduct produced by the Bayer process used to obtain alumina from bauxite. Research by Samouhos et al. [1] studies that red mud is reasonably basic (pH = 10–13) and contains a variety of minerals such as Ba, Ca, Cd, Cr, Fe, Hf, K, Mg, Na, Ni, Pb, Si, Sr, Nd, Th, U, V, and Zn. Red mud is discarded at disposal sites; however, proper treatment methods are unestablished adequately due to its detrimental qualities, which include high alkalinity and metal toxicity, as well as their impact on the ecosystem [2,3]. Numerous studies have been conducted to determine how to stabilize and utilize red mud as adsorbents, building materials, and catalysts [2,4].

Although red mud is predominantly composed of Fe, Al, Si, Na, Ca, and Ti, it also contains trace elements such as valuable metals and rare earth elements (REEs), including Ga, V, Zr, Sc, Cr, Mn, Y, Ni, Zn, Th, and U [5,6]. Several studies on red mud as a secondary source for regaining important compounds via various extraction processes have been done [7–15]. Hydrometallurgical and bioleaching methods were utilized in these studies to extract elements from red mud [12,16–26]. In controlled autoclave reactors, solvents were also employed to recover important components from red mud, including sulfuric

acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), and other selective reagents such as cyanex and di [2-ethylhexyl] phosphoric acid. However, intense acid solutions are required for solvent extraction to maximize the element recovery, resulting in a high concentration of hazardous contaminants through the extracted solution, which must be treated as effluent [13].

In addition, pyrometallurgical methods, including the reductive-roasting process, were utilized to recover essential substances from a variety of materials such as red mud and steel furnace slag, in order to improve element selectivity. Magnetic separation of reduced iron obtained during the reductive roasting process was followed by extraction of other valuable components using solvents under various circumstances [13,27–34]. Hover et al. [16] examined the retrieval of Co, Cu, and Ni from seawater manganese nodules utilizing carbon through the reductive-roasting process as a reducing agent and a variety of chlorides (NaCl , CaCl_2 , NH_4Cl , LiCl , and CsCl) as chlorinating agents. They discovered that Co, Cu, and Ni could be recovered selectively at different roasting temperatures (1050 °C for Co and Ni; 850 °C for Cu). Additionally, the chlorinating agents type had an effect on substance recovery and selectivity ($\text{CaCl}_2 > \text{NH}_4\text{Cl} > \text{other agents}$). Borra et al. [13] described the selective retrieval of REEs from red mud by pyrometallurgical techniques (i.e., sulfation, roasting, and leaching). Leaching tests on roasted red mud were undertaken under different leaching conditions (solvent, leaching temperature, and time). The results indicated that the recovery and selectivity of elements varied according to roasting and leaching conditions.

Microwaves have been utilized as a heat source to recover precious metals from natural resources, including heavy metals including Al, Co, Cu, Pb, Ni, Mg, and Zn, and REEs such as Ce, La, Sc, Nd, and Sm. Microwave pretreatment increases metal recovery and reduces process time [24,35–38]. Although most researchers who have undertaken microwave-assisted leaching have employed acid solutions as additives to leach metals from raw materials, a few have made use of solid salts. Kruesi and Frahm [35] presented a microwave-assisted leaching process for extracting metals (Co, Ni, and Mn) from laterite ores utilizing ferric and sodium chlorides as additives. For that research, ores were combined with ferric chloride (FeCl_3) and sodium chloride (NaCl) and microwaved for 4–8 min at 2.45 GHz and 600 W, followed by leaching with water. This approach is analogous to the reductive roasting processes in which carbon and chloride salt are used to remove components from insoluble materials through roasting, reduction, and leaching. Kim et al. [38] recently developed a microwave-assisted leaching method for extracting Ca and Na from red mud utilizing solid NH_4Cl as an additive. They demonstrated that adding solid NH_4Cl to the red mud throughout the microwave heating process effectively leached calcium and sodium at the high microwave output power of 5000 W.

In the present study, solid NH_4Cl as a chlorinating agent was used during the microwave heating of red mud (i.e., roasting process) to improve the recovery of trace elements, selectively, during the metal-leaching processes. This is because NH_4Cl easily decomposes in heat and produces NH_3 and HCl gases, which enhance reactive conditions during microwave heating processes. No carbon was added as a reducing agent or microwave receptor. The purpose of this study was to investigate selective leaching of valuable trace elements from red mud, microwave-heated with and without the addition of solid NH_4Cl . The red mud slurry having a moisture content of about 30% and dried red mud with the addition of solid NH_4Cl were heated under various conditions (i.e., microwave output power and microwave heating time). The microwave-heated red mud was then used in the leaching tests using deionized (DI) water as a solvent.

2. Materials and Methods

2.1. Material

Red mud was obtained from Dae Bul industrial complex, Jeollanam-do Province, Korea. Total elements of the as-received red mud were analyzed by using U.S. EPA Method 3051A (U.S. Environmental Protection Agency, Washington, DC, USA) for total element

analysis at the National Instrumentation Center for Environmental Management (NICEM, Seoul, South Korea). The as-received red mud might be partially dissolved in concentrated nitric acid and concentrated hydrochloric acid by microwave heating using a suitable laboratory microwave oven. After dissolution of red mud in concentrated nitric acid and concentrated hydrochloric acid, major elemental concentrations (Na, K, Ca, Mg, Al, and Fe) were measured by an inductively coupled plasma–atomic emission spectrometer (ICP-AES) (Optima 3000XL, Perkin-Elmer, Wellesley, MA, U.S.A.) and minor elemental concentration (V, Cr, Mn, Ni, Co, Ga, Pb, Zn, Ba, As, Cu, and Mo) were measured by an inductively coupled plasma mass spectrometer (ICP-MS) (Elan DRC II, Perkin-Elmer, Wellesley, MA, USA).

The major elements were contained in the as-received red mud in the following order: Fe > Al > Na > Ca > Mg > K. The red mud also contained other trace elements in the following order: V > Cr > Mn > Ni > Co > Ga > Pb > Zn > Ba > As > Cu > Mo (Table 1). The mineralogical composition of the red mud was obtained using X-ray diffraction (XRD) (D8 Venture, Bruker, Billerica, MA, USA) analysis at KBSI (Seoul, South Korea). The results of X-ray diffraction (XRD) analysis showed that the red mud was primarily composed of hematite (Fe_2O_3), boehmite ($\text{AlO}[(\text{OH})]$), ilmenite (FeTiO_3), quartz (SiO_2), and sodium aluminosilicate hydrate ($\text{Na}_6(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$) (Figure 1). The analytical reagent-grade NH_4Cl (99.5 wt.%, Junsei Chemical Co., Ltd., Tokyo, Japan) was used as a chlorinating agent during microwave heating for selective leaching of valuable trace elements. DI water was used as a solvent in the leaching tests.

Table 1. Results of total elemental analysis for the as-received red mud.

Material	Elemental Composition (mg/kg)					
	Al	Fe	Ca	Na	Mg	K
As-received red mud	58,124	99,045	17,191	47,083	267	209
	Si	As	Ga	V	Cr	Pb
	80	7.5	16.9	229.9	176.3	16.7
	Mn	Zn	Ni	Cu	Co	Ba
	145.8	12.9	23.3	4.7	17.1	8.2

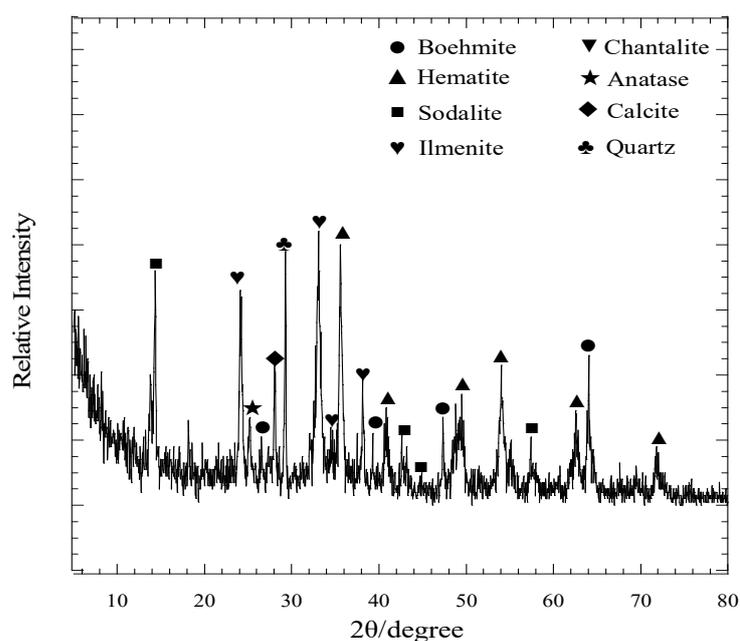


Figure 1. Results of XRD analysis for the as-received red mud.

2.2. Methods

A red mud sample with approximately 30% water content (i.e., red mud slurry) or a mixture of dried red mud and solid NH_4Cl (i.e., red mud-solid NH_4Cl) were placed in a heat-resistant ceramic container and heated with microwave ovens for various times (i.e., 5, 10, 15, or 20 min). Schematic of the experimental process is shown in Figure 2.

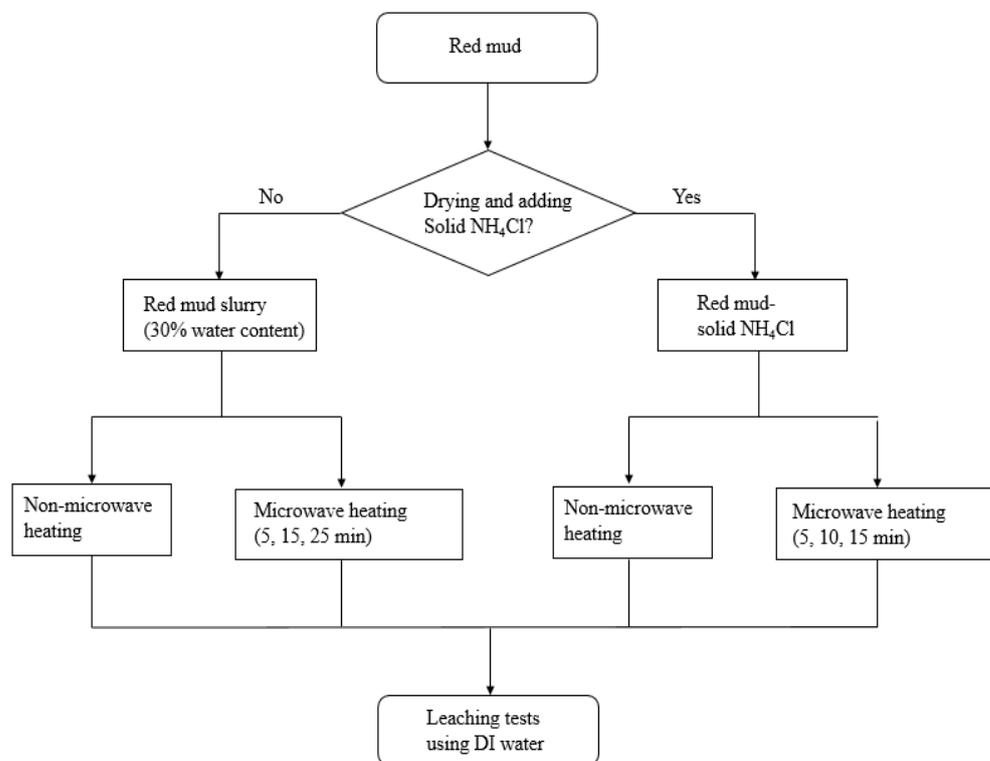


Figure 2. Schematic of the experimental process.

As-received red mud samples with residual water were dried at 105 °C in an oven for 48 h. The dried red mud was then mixed with solid NH_4Cl (10:1 weight ratio, i.e., red mud sample with the addition of solid NH_4Cl). A fixed weight ratio (10:1) was used in the present study because Jo et al. [39] reported that the concentration of ammonium salt solutions had a slight effect on the alkaline earth metal leachability of waste material (i.e., waste slate). However, it should be noted that the weight ratio might affect the results of the present study. The red mud with solid NH_4Cl was placed in a heat-resistant ceramic container and were then heated with household microwaves at different output powers (i.e., 500 and 1100 W) and the same frequency (2.45 GHz). The red mud with solid NH_4Cl were placed in an alumina crucible and then heated with an industrial microwave at 5000 W output power. An alumina crucible was used because red mud could be elevated to more than 1000 °C by high power microwaves. In addition, the red mud with approximately 30% water content (i.e., red mud slurry) was microwave-heated under the same conditions that the dried red mud with the addition of solid NH_4Cl (i.e., red mud–solid NH_4Cl) were microwave-heated.

Immediately after microwave heating, the red mud was melted and emitted black gases. After cooling down the red mud sample, the solidified hard parts were collected for the leaching test. For the leaching tests, each of the red mud samples heated with microwaves was mixed with DI water (pH = 5.6) at a solid dosage of 100 g/L and stirred at 300 revolutions per minute (rpm) at room temperature (approximately 25 °C) for 24 h. The solid dosage of 100 g/L was used because no significant solid dosage effect on the leachability was observed in the previous study [38]. To evaluate the effects of microwave heating, the leaching tests were also conducted on the non-microwave-heated red mud

with approximately 30% water content (i.e., red mud slurry) and a non-microwave-heated red mud with the addition of solid NH_4Cl (i.e., red mud-solid NH_4Cl). After the leaching tests, the mixtures were filtered using a 0.2 μm filter (ADVENTEC[®], Ontario, Canada) to separate the solid and leachate. The element concentrations of the filtered leachate were measured by ICP-MS (Elan DRC II, Perkin-Elmer, Wellesley, MA, USA) at Korea Basic Science Institute (KBSI).

3. Results and Discussion

3.1. Elements Leached from Microwave-Heated Red Mud Slurry without the Addition of Solid NH_4Cl

Trace element concentrations leached from non-microwave-heated and microwave-heated red mud slurry and red mud-solid NH_4Cl under various test conditions are summarized in Table 2. Figure 3 shows the Cr, V, As, Fe, Co, Cu, Mn, Ni, Pb, and Zn concentrations leached from the microwave-heated red mud samples without the addition of solid NH_4Cl . Larger amounts of V, Cr, and As were leached from the microwave-heated red mud slurry than from both the non-microwave-heated red mud slurry and the microwave-heated red mud-solid NH_4Cl , regardless of the test conditions. In contrast, a significantly less amount of Co, Cu, Mn, Ni, Pb, and Zn were leached from the microwave-heated red mud slurry than from the non-microwave-heated red mud slurry, except for Zn from microwave-heated red mud slurry at 500 W for 5 min (Figure 3).

Table 2. Element concentrations leached from microwave-heated red mud slurry and red mud-solid NH_4Cl samples.

Sample	Solvents	Solid-to-Liquid Ratio (g/L)	Output Power (W)	Pretreatment Time (min)	Concentration ($\mu\text{g}/\text{kg}$)											
					Cr	V	As	Co	Cu	Mn	Ni	Pb	Zn			
Red mud slurry	DI water	100	-	0	380	530	110	30	420	40	260	< ^a 1	440			
Red mud-solid NH_4Cl	DI water	100	-	0	410	470	130	40	2250	<1	310	<1	1380			
Red mud slurry	DI water	100	500	5	1640	72,300	5440	40	123	<1	82	<1	1320			
				15	2420	99,480	7030	19	186	<1	25	<1	470			
				25	3400	95,100	6340	19	213	<1	16	<1	<1			
				1100	5	2160	61,600	3830	17	110	<1	19	<1	44		
					15	8850	71,700	4760	16	176	<1	27	<1	285		
					25	24,500	74,800	4030	0	123	<1	13	<1	<1		
			5000	5	5050	128,000	9550	30	332	<1	33	<1	<1			
				15	50,300	143,000	2430	0	29	<1	0	<1	<1			
				25	37,600	158,000	2750	0	108	<1	0	<1	<1			
			Red mud-solid NH_4Cl	DI water	100	500	5	1720	3150	262	33	455	<1	94	12	147
							10	1520	3330	194	31	503	<1	121	<1	134
							15	1660	3130	176	31	398	<1	135	<1	704
1100	5	1280					952	204	16	267	<1	124	<1	110		
	10	731					2260	<1	29	263	<1	130	<1	127		
	15	566					1480	<1	105	280	<1	445	<1	426		
5000	5	50				632	17	60	591	168	223	<1	<1			
	10	30				204	66	5170	6590	157,000	4470	3660	3650			
	15	98				215	97	7990	10,900	251,000	5990	3070	7350			

<^a 1: non-detectable.

In the microwave-heated red mud slurry, the leached element concentrations were higher at a given heating condition in the following order: $\text{V} > \text{Cr} > \text{As}$ (Figure 3). This is comparable to the total element concentrations of the as-received red mud sample (Table 1). These results suggest that the microwave heating on the red mud slurry is effective for leaching V, Cr, and As, but is not effective for leaching Co, Cu, Mn, Ni, Pb, and Zn.

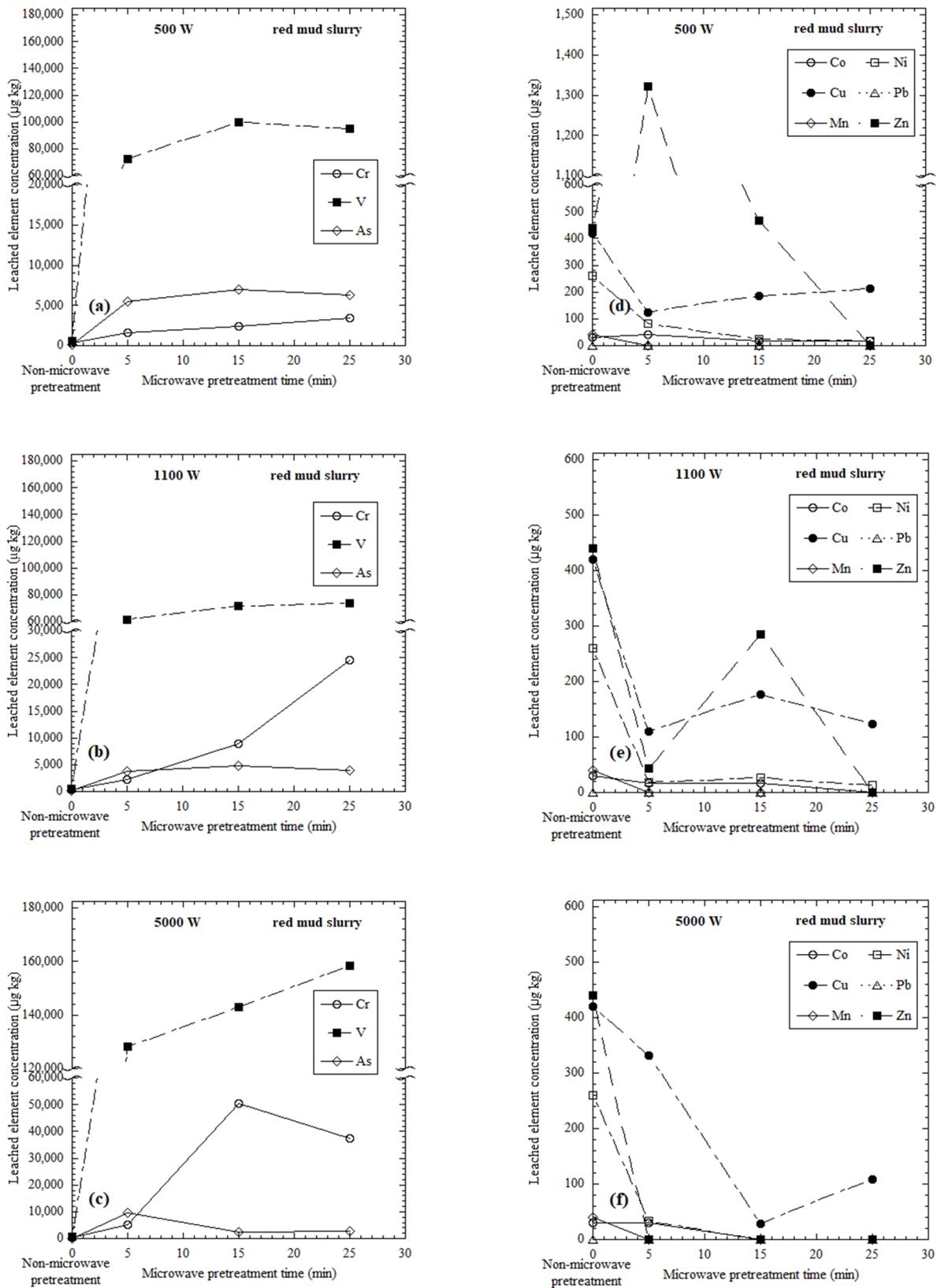


Figure 3. Cr, V, and As leached concentrations at various output powers: (a) 500 W, (b) 1100 W, and (c) 5000 W and Co, Cu, Mn, Ni, Pb, and Zn leached concentrations at various output powers: (d) 500 W, (e) 1100W, and (f) 5000 W from the red mud slurry microwave-pretreated at various output powers.

For the red mud slurry, the leached Cr, V, and As concentrations increased with a longer heating time at a given output power, and with increasing the output power at a given heating time (Figure 3). For example, the leached V concentration from microwave-heated red mud slurry increased from 72,330 to 95,098 $\mu\text{g}/\text{kg}$ when heating time increased from 5 to 25 min at an output power of 500 W, and from 95,098 to 158,256 $\mu\text{g}/\text{kg}$ as the output power increased from 500 to 5000 W at the heating time of 25 min (Figure 3). These results suggest that the output power and heating time significantly affect Cr, V, and As leaching from the microwave-heated red mud slurry. However, the leached V concentration from the non-microwave-heated red mud slurry was significantly low (530 $\mu\text{g}/\text{kg}$). In contrast to Cr, V, and As, little to no amounts of Mn, Cu, Co, Zn, Ni, and Pb were leached from the microwave-heated dried red mud without solid NH_4Cl (Figure 3 and Table 2), indicating microwave heating had no effect on their leachability. At 5000 W, red mud can be heated to 321 $^\circ\text{C}$ after only 5 min of microwave treatment and heated to approximately 1600 $^\circ\text{C}$ after 25 min of microwave treatment [38]. The increase in temperature can be sufficient to cause changes in mineral phases of red mud. Mn, Cu, Co, Zn, Ni, and Pb may be converted to oxide forms during microwave heating, resulting in a decrease in their solubility.

3.2. Elements Leached from Microwave-Heated Dried Red Mud with the Addition of Solid NH_4Cl

In contrast to the microwave-heated red mud slurry, smaller amounts of V, Cr, and As were leached from the microwave-heated red mud-solid NH_4Cl than the microwave-heated red mud slurry, regardless of the test conditions. However, a slightly larger amount of V, Cr, and As was leached from the microwave-heated red mud-solid NH_4Cl at 500 W than the non-microwave-heated red mud-solid NH_4Cl (Figure 4 and Table 2). Larger amounts of Co, Cu, Mn, Ni, Pb, and Zn were leached from the red mud-solid NH_4Cl that were microwave-heated at 5000 W for more than 10 min, than from both the non-microwave-heated red mud samples and microwave-heated red mud slurry. In the red mud-solid NH_4Cl that were microwave-heated at 5000 W, the leached element concentrations were higher at a given heating time in the following order: $\text{Mn} > \text{Cu} > \text{Co} > \text{Zn} > \text{Ni} > \text{Pb}$ (Figure 4). This is comparable to the total element concentrations of the as-received red mud (Table 3). These results suggest that the microwave heating on the red mud-solid NH_4Cl is effective for leaching the Mn, Cu, Co, Zn, Ni, and Pb, but it is not effective for leaching V, Cr, and As.

Table 3. Optimal conditions for the maximum element recovery from the red mud.

Element	Optimal Conditions			Leaching Efficiency (%)
	Solid NH_4Cl	Output Power (W)	Pretreatment Time (min)	
V	No	5000	25	69.0
Cr	No	5000	15	18.2
As	No	5000	5	100
Mn	Yes	5000	15	100
Cu	Yes	5000	15	100
Co	Yes	5000	15	46.7
Zn	Yes	5000	15	57.0
Ni	Yes	5000	15	25.7
Pb	Yes	5000	15	18.4
Fe	Yes	5000	15	9.4

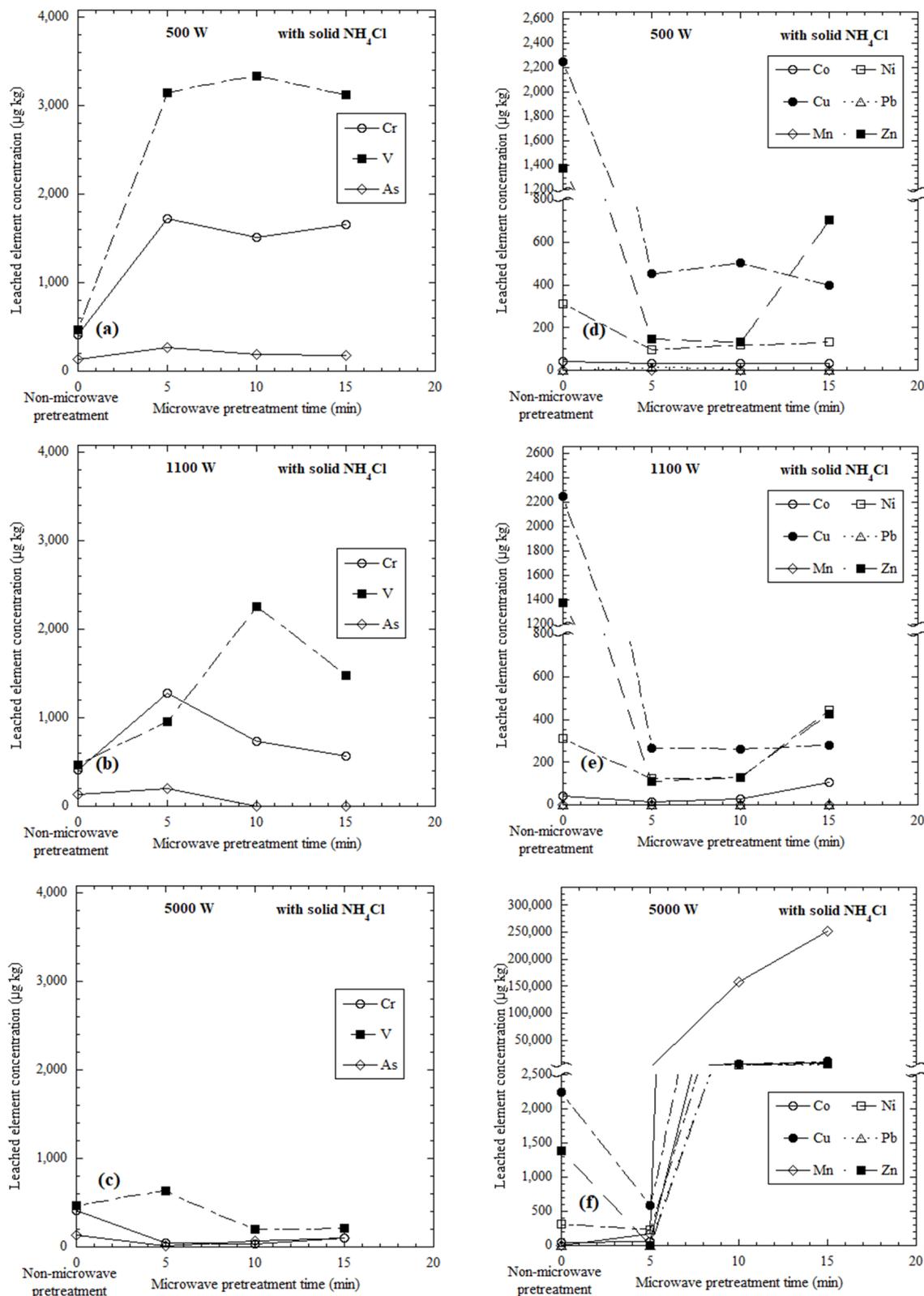


Figure 4. Cr, V, and As leached concentrations at various output powers: (a) 500 W, (b) 1100 W, and (c) 5000 W and Co, Cu, Mn, Ni, Pb, and Zn leached concentrations at various output powers: (d) 500 W, (e) 1100 W, and (f) 5000 W from the red mud-solid NH₄Cl microwave-pretreated at various output powers.

For the red mud-solid NH₄Cl, the significantly high concentrations of leached Mn, Cu, Co, Zn, Ni, and Pb were obtained at 5000 W for more than 10 min. Little to no amounts of

Mn, Cu, Co, Zn, Ni, and Pb were leached at 500 and 1100 W, indicating that the microwave heating on the red mud-solid NH_4Cl was only effective at 5000 W for more than 10 min (Figure 4). For example, the leached Mn concentration from the microwave-heated red mud-solid NH_4Cl increased from 157,214 to 251,102 $\mu\text{g}/\text{kg}$ as the heating time increased from 10 to 15 min at the output power of 5000 W. These results suggest that trace elements from red mud can be sequentially extracted. As, Cr, and V can be extracted from red mud slurry by microwave heating at 5000 W for 5, 10, and 15 min, respectively. The other trace elements can be extracted from red mud by microwave heating at 5000 W for 15 min after adding NH_4Cl solid to red mud. However, the sequential extraction of trace elements is required for validation.

3.3. Discussion of Selective Leaching from Microwave-Heated Red Mud

For V, Cr, and As, the highest leaching efficiencies were obtained from the microwave heated red mud slurry at 5000 W for different heating times (V: 69.0% for 25 min; Cr: 13.6% for 15 min; As: 36.6% for 5 min; Table 3). On the other hand, from the microwave heated red mud slurry, almost no Mn, Cu, Co, Zn, Ni, and Pb were leached. These results suggest that V, Cr, and As can be selectively leached from the microwave-heated red mud without the addition of a chlorinating agent (i.e., solid NH_4Cl). The fraction of V, Cr, and As in the leached solutions may be controlled by changes in the microwave heating conditions (e.g., output power and heating time).

In contrast, for Mn, Cu, Co, Zn, Ni, and Pb, the highest leaching efficiencies were obtained from the microwave-heated red mud-solid NH_4Cl at 5000 W for a longer heating time (15 min; Figure 5). In particular, Mn and Cu were completely leached at 5000 W for more than 10 min (Table 3 and Figure 5). The leaching efficiency for Mn and Cu exceeded 100%. The exact reason is unknown, but the elemental composition of as-received red mud might be underestimated because silica contained in the as-received red mud was partially dissolved in the strong acid solution during total elemental analysis. Semi-quantitative mineral phase analysis results using the Rietveld method of the as-received red mud indicated that approximately 8.8% of silica was contained in the as-received red mud (Table 4), but the trace amount of Si (80 mg/kg) was dissolved during the total elemental analysis process (Table 1). On the other hand, almost no V, Cr, and As were leached from the microwave-heated red mud-solid NH_4Cl . These results suggest that the microwave heating of red mud with the addition of a chlorinating agent (i.e., solid NH_4Cl) is effective for the selective leaching of Mn, Cu, Co, Zn, Ni, and Pb from the red mud.

Red mud can be composed of various minerals that are either active or inactive in the microwave. Active material in the microwave is rapidly heated, and inactive material is very slowly heated. The microwave-active materials contained in the red mud can potentially be heavy-metal bearing minerals (e.g., Co-, Mn-, and Ni-bearing oxide minerals, hematite, or magnetite). When the red mud samples were microwave-heated, the microwave-active minerals (e.g., hematite, magnetite, or the Co-, Mn-, and Ni-bearing oxide minerals) contained in the red mud were quickly heated, resulting in high temperature [40]. Water-insoluble V-, Cr-, and As-bearing minerals in red mud can be decomposed and transformed to water soluble V-, Cr-, and As-bearing oxides during microwave heating of red mud slurry, resulting in higher leaching efficiency for red mud slurry. After the roasting of red mud samples with the addition of solid NH_4Cl induced by microwave irradiating, V-, Cr-, and As-bearing oxide minerals might be volatilized or decomposed and transformed to V, Cr, and As chloride compounds. The V, Cr, and As chloride compounds have low solubility in water and high boiling points [41], resulting in their low leached concentrations (Table 2). The red mud could be heated to approximately 320–1600 °C after microwave heating of 5–15 min [38]. The red mud-solid NH_4Cl were placed in an alumina crucible and then heated with microwaves at 5000 W output powers. Microwaves can be trapped inside of an alumina crucible, leading to very high temperature. The increase in temperature of the red mud is sufficient to cause a change in the mineral phases. As the

microwave-output power increased, the temperature increased rapidly and substantially, easing chlorination and evaporation, which resulted in the significant decrease in the leached concentrations. Recently, Khattak et al. [41] suggested the principle of microwaves trapped in a spherical grape to produce plasma. They explained that microwaves were trapped inside of a grape because the wavelength of the microwaves and the diameter of a grape was similar. The temperature in the center of the grapes rose rapidly due to microwaves trapped in the grapes. Similar to the Khattak's results [41], the microwave irradiated inside the aluminum crucible could be constantly reflected from the inside, and the temperature of the red mud placed in the center of the crucible could rise rapidly.

Table 4. Semi-quantitative mineralogical analysis results using the Rietveld method of microwave-heated red mud-solid NH_4Cl at 5000 W.

Mineral	Chemical Formula	As Received Red Mud	Red Mud-Solid NH_4Cl		
		wt. %	Microwave Heating Time at 5000 W		
			wt. %	wt. %	wt. %
Sodium aluminum silicates	$\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{14.35}$	21	5	^a n.d.	<1
Sodalite	$\text{ClNa}_4\text{Al}_3\text{Si}_3\text{O}_{12}$	7	8	<1	n.d.
Hematite	Fe_2O_3	22	26	7	10
Quartz	SiO_2	9	7	6	2
Chantalite	$\text{CaAl}_2\text{SiO}_8\text{H}_4$	<1	n.d.	n.d.	n.d.
Calcite	CaCO_3	6	3	<1	<1
Boehmite	AlOOH	16	14	<1	<1
Anatase	TiO_2	4	5	1	<1
Nosean	$\text{CNa}_8\text{Al}_6\text{Si}_6\text{O}_{27}$	3	<1	<1	n.d.
Ilmenite	FeTiO_3	11	n.d.	n.d.	n.d.
Halite	NaCl	n.d.	19	30	25
Labradorite	$\text{Na}_{0.35}\text{Ca}_{0.65}\text{Al}_{1.65}\text{Si}_{2.35}\text{O}_8$	n.d.	n.d.	20	24
Spinel	FeAl_2O_4	n.d.	2	7	12
Corundum	Al_2O_3	n.d.	<1	11	6
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	n.d.	1	3	6
Maghemite	$\gamma\text{Fe}_2\text{O}_3$	n.d.	<1	<1	2
Cristobalite	SiO_2	n.d.	2	2	3
Albite	$\text{NaAlSi}_3\text{O}_8$	n.d.	n.d.	4	4
Rutile	TiO_2	n.d.	3	5	4
Magnetite	Fe_3O_4	n.d.	1	<1	<1
Total	-	99	96	95	98

^a n.d.: non-detectable.

In contrast, little to no Mn, Cu, Co, Zn, Ni, and Pb leached from the non-microwave-heated and microwave-heated red mud-solid NH_4Cl , at either at 500 or 1100 W. The leached concentrations significantly increased in the microwave-heated red mud-solid NH_4Cl at 5000 W for more than 10 min. The oxides of Mn, Cu, Co, Zn, Ni, and Pb could be rapidly heated by microwave irradiating, as these oxides were microwave-active metals and insoluble in water [41]. However, the metal oxides could not be easily reduced because no carbon was added to the red mud during microwave-heating in the present study. On the other hand, after microwave heating of the red mud-solid NH_4Cl at a high output power of 5000 W, Mn-, Cu-, Co-, Zn-, Ni-, and Pb-bearing oxide minerals were decomposed and transformed into metal chloride compounds. After metal oxides were chlorinated, the metals could be recovered from the microwave-heated red mud-solid NH_4Cl by leaching processes using DI water. All of the chloride forms of Co, Cu, Mn, Ni, Pb, and Zn are relatively soluble in water [42], resulting in relatively higher leaching efficiencies. In particular, the Mn leaching efficiency was higher than the other metals, because Mn oxides have a relatively lower melting point [42], resulting in higher chlorination.

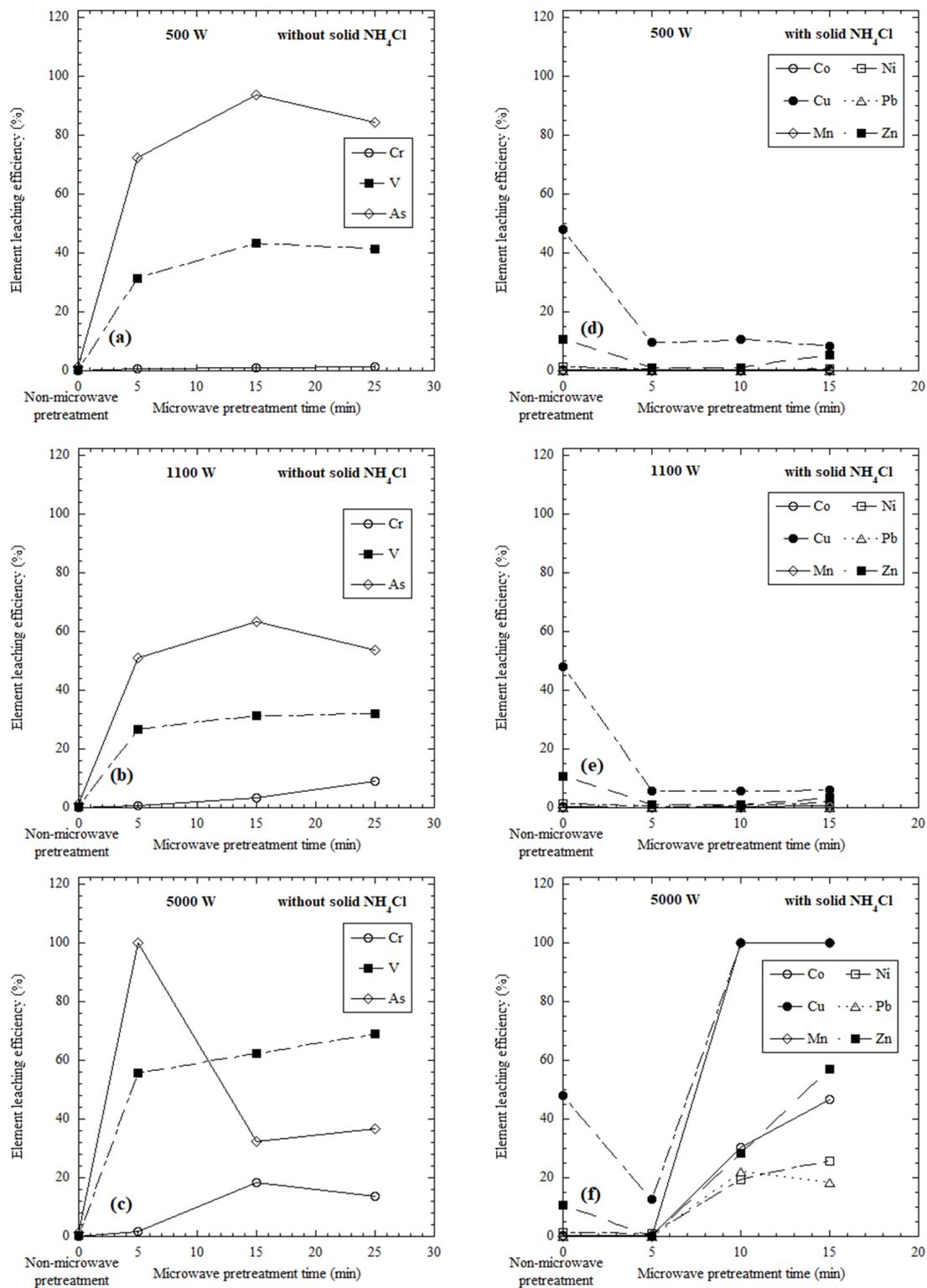


Figure 5. Cr, V, and As leaching efficiency at various output powers: (a) 500 W, (b) 1100 W, and (c) 5000 W and Co, Cu, Mn, Ni, Pb, and Zn leaching efficiency at various output powers: (d) 500 W, (e) 1100 W, and (f) 5000 W from the red mud-solid NH₄Cl microwave-pretreated at various output powers.

Semi-quantitative mineral phase analysis results using the Rietveld method of microwave-heated red mud-solid NH₄Cl at 5000 W are summarized in Table 4. The cancrinite (Na₄Al₃Si₃O_{14.35}), sodalite (ClNa₄Al₃Si₃O₁₂), and calcite (CaCO₃) contents decreased, whereas the labradorite (Na_{0.35}Ca_{0.65}Al_{1.65}Si_{2.35}O₈) content increased with increasing the

microwave heating time. In addition, the hematite (Fe_2O_3), boehmite (AlOOH), and ilmenite (FeTiO_3) contents decreased, and spinel (FeAl_2O_4), corundum (Al_2O_3), rutile (TiO_2), and halite (NaCl) were newly formed. Traces of magnetite (Fe_3O_4) were also observed. These results suggest that mineral phase changes and chlorination occurred in the red mud–solid NH_4Cl during microwave heating. These mineral phase changes and chlorination, which might cause the selective leaching of trace elements. However, the mechanism of the selective leaching of trace elements from red mud with and without solid NH_4Cl during microwave heating should be verified using various mineral phase analysis techniques.

Figure 6 shows the SEM images of the red mud heated with microwaves. Figure 6a,b are the SEM images of red mud slurry heated with microwaves for 5 min and 15 min at 5000 W. Figure 6c,d are the SEM images of red mud–solid NH_4Cl heated with microwaves for 10 min and 15 min at 5000 W. Comparing Figure 6a,b and Figure 6c,d, the SEM image of Figure 6c shows that a relatively large crystal was newly formed. In Figure 6d, amorphous minerals appear to have formed after the minerals in the red mud melted. Amorphous minerals shown in Figure 6d could be easily dissolved during leaching process after microwave heating because amorphous minerals have low stability than previous crystal.

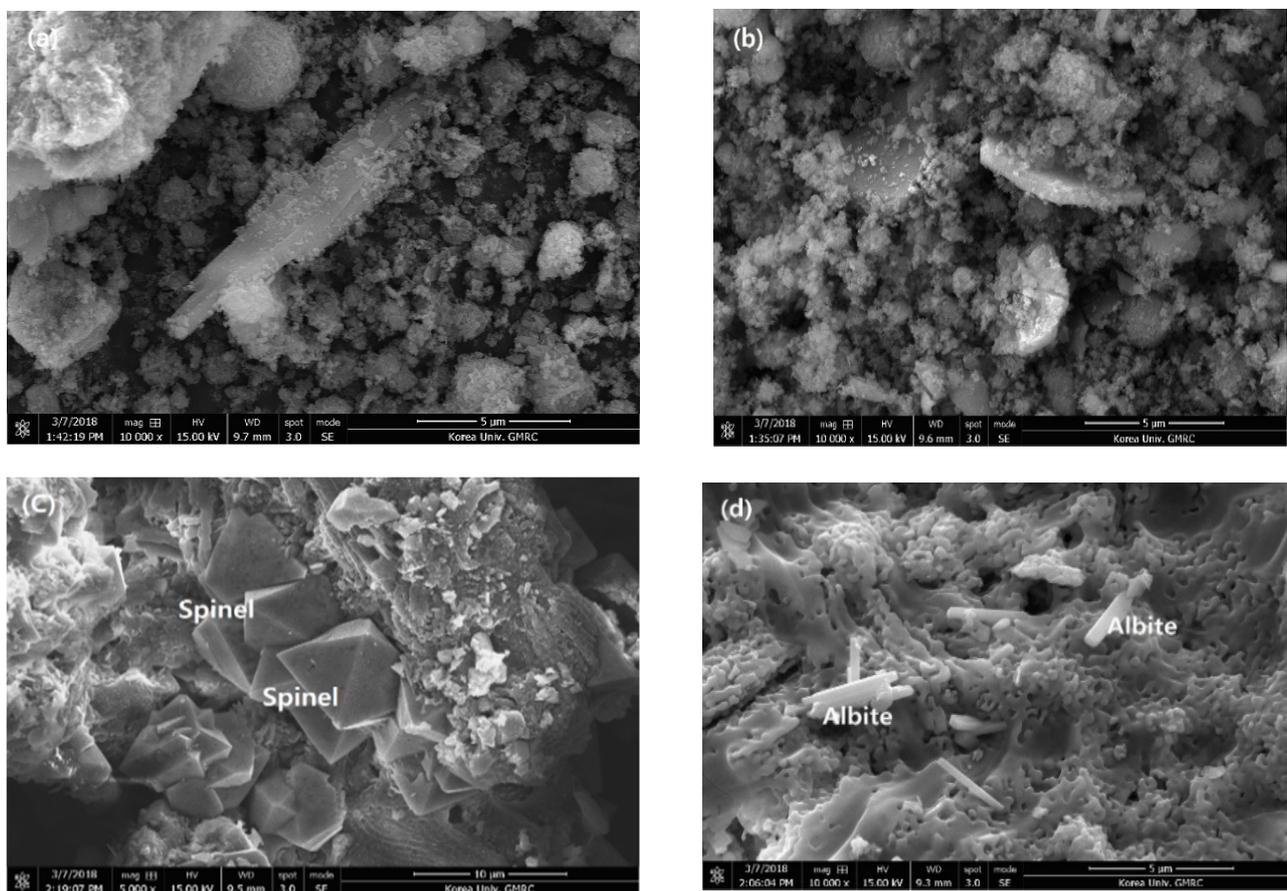


Figure 6. SEM images of the red mud heated with microwaves: (a,b) are the red mud slurry heated with microwaves for 5 min and 15 min at 5000 W; (c,d) are the red mud–solid NH_4Cl heated with microwaves for 10 min and 15 min at 5000 W.

4. Conclusions

Red mud was heated using microwave ovens under various conditions (i.e., presence of chlorinating agent: NH_4Cl , output power, and heating time) to evaluate the effect of microwave heating on the leachability and selectivity of trace elements from red mud. Leaching tests were then conducted using DI water on the microwave-heated red mud without or with solid NH_4Cl . V, Cr, and As were selectively leached from the microwave-

heated red mud without adding solid NH_4Cl in the following order at a given heating condition: $\text{V} > \text{Cr} > \text{As}$, and Mn, Cu, Co, Ni, Zn, and Pb were selectively leached from the microwave-heated red mud with adding solid NH_4Cl in the following order at a given heating condition: $\text{Mn} > \text{Cu} > \text{Co} > \text{Zn} > \text{Ni} > \text{Pb}$.

The highest leaching efficiencies for V, Cr, and As were obtained from the microwave heated red mud without the addition of solid NH_4Cl at 5000 W for different heating times (V: 25 min; Cr: 15 min; As: 5 min). However, after microwave heating the red mud–solid NH_4Cl almost no V, Cr, or As were leached. In contrast, after microwave-heating the red mud samples without the addition of solid NH_4Cl , almost no Mn, Cu, Co, Zn, Ni, or Pb were leached. However, the highest leaching efficiencies for Mn, Cu, Co, Zn, Ni, and Pb were obtained from the microwave-heated red mud samples by adding solid NH_4Cl at 5000 W for a longer heating time (15 min).

The results of present study suggest that V, Cr, and As can be selectively leached from the microwave-heated red mud without the addition of a chlorinating agent (i.e., solid NH_4Cl). The microwave heating of red mud with the addition of a chlorinating agent (i.e., solid NH_4Cl) is effective for selective leaching Mn, Cu, Co, Zn, Ni, and Pb from the red mud. The element selectivity can be controlled by changes in the microwave heating conditions (e.g., output power and heating time). The results of a small amount of Fe leaching suggest that microwave heating of red mud is effective for leaching trace elements without the process of separating Fe from red mud such as reductive-roasting process. However, further research is needed to discover the mechanisms and optimal conditions for selective leaching using microwave heating of red mud with or without the addition of solid NH_4Cl as a chlorinating agent.

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Conflicts of Interest: The authors declare no conflict of interest.

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