

Article

# Leaching Process of Rare Earth Elements, Gallium and Niobium in a Coal-Bearing Strata-Hosted Rare Metal Deposit—A Case Study from the Late Permian Tuff in the Zhongliangshan Mine, Chongqing

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**Abstract:** The tuff, a part of coal-bearing strata, in the Zhongliangshan coal mine, Chongqing, southwestern China, hosts a rare metal deposit enriched in rare earth elements (REE), Ga and Nb. However, the extraction techniques directly related to the recovery of rare metals in coal-bearing strata have been little-studied in the literature. The purpose of this paper is to investigate the extractability of REE, Ga and Nb in the tuff in the Zhongliangshan mine using the alkaline sintering-water immersion-acid leaching (ASWIAL) method. The results show that ASWIAL can separate and extract REE, Ga and Nb effectively under the optimized conditions of calcining at 860 °C for 0.5 h with a sample to sintering agent ratio of 1:1.5, immersing at 90 °C for 2 h with 150 mL hot water dosage, and leaching using 4 mol/L HCl at 40 °C for 2 h with a liquid-solid ratio of 20:1 (mL:g). The final leaching efficiencies of REE and Ga are up to 85.81% and 93.37%, respectively, whereas the leaching efficiency of Nb is less than 1%, suggesting the high concentration of Nb in the leaching residue, which needs further extraction.

**Keywords:** extractability; alkaline sintering-water immersion-acid leaching; tuff; Chongqing

## 1. Introduction

The study of rare metal deposits hosted in coal-bearing strata is currently one of the research hotspots in the field of coal geology. The term “metalliferous coal” has been widely adopted to describe coal anomalously enriched in trace metals with potential economic and practical value for rare metal recovery [1–11]. From the perspective of industrial production, coal can be considered as metalliferous at the level of trace element concentrations being at least 10 times greater than the corresponding averages of world coal [1]. Many studies have shown that not only coal but some of the non-coal rock strata within or adjacent to the coal seams are also enriched in various valuable metals [8,12–14]. Due to the gradual depletion of many conventional rare metal ores and the difficulties in exploring new deposits, alternative rare metal sources are urgently needed to be discovered and exploited [7,8]. Furthermore, with respect to the increasing challenges of global warming and other environmental issues, the utilization of coal resources is increasingly encouraged to be economically effective and environmentally benign [2,3]. Hence, some coal-bearing strata have been regarded as promising alternative sources for rare metals recovery, to which many researchers around the world have paid great attention in recent years [1–15]. There are already some precedents in the case of rare metal extraction from coal and coal-related materials. For example, germanium is

currently being recovered mainly from three well-known Ge-bearing coal deposits, namely Lincang (Yunnan province) and Wulantuga (Inner Mongolia) of China, as well as Spetzugli of eastern Russia, which account for more than 50% of the total yearly production of Ge metal in the world [3,7,9,11]. The discovery of a super-large coal-hosted gallium and aluminum deposit in the Jungar Coalfield (Inner Mongolia), China is another example [16], which was highly recognized and considered as the third most significant and outstanding discovery for coal-hosted metal deposit production following the successful industrial extractions of uranium and germanium from coal [5,17]. Recently, a new type of Nb (Ta)-Zr (Hf)-REE-Ga polymetallic ore deposit was discovered in the late Permian coal-bearing strata of eastern Yunnan, southwestern China [14], and some other types of elemental assemblages have also been observed in coalfields in southern China [7,8,18,19].

The mechanisms of rare-metal mineralization have been discussed in detail in substantial studies [1,3,4,7–9,13,19], some of which have also highlighted the geologic and tectonic controls on the localization of metalliferous coal deposits [8]. However, extraction techniques directly related to the recovery of rare metals from coal deposits, which are undoubtedly the critical issue for metalliferous coal uses, have been paid less attention in the literature. At present, the possible recovery of rare metal elements from coal-bearing strata and coal combustion products (CCPs) is an exciting research area, since coal and particularly its combustion derivations may have elevated concentrations of metal elements that are comparable to or even higher than those found in conventional metal ores [5,20–27]. For this reason, the U.S. Department of Energy's National Energy Technology Laboratory (NETL) funded 10 projects in 2015 aiming to support the lab's research program on the recovery of REE from coal and coal byproducts [28].

Learnings from the metallurgy of conventional ores can be applied to metalliferous coal [29–31]. For example, scientists from the U.S. Department of Energy, inspired by the traditional hydrometallurgical method of ion exchange, carried out a series of lab-scale REE extraction tests using ammonium sulfate, an ionic liquid and a deep eutectic solvent as lixiviants, and produced a marked extraction efficiency of REE at least from the selected coal byproducts [32]. Acid leaching incorporated with acid/alkali sintering is a common metallurgical process for metal extraction [33,34], and has been a major technology applied to the recovery of metals like alumina from coal fly ash [35]. As compared with solely resorting to hydrogen fluoride (HF) digestion, which may be too hazardous for large-scale industrial use, pretreatment with an alkaline agent could effectively liberate REE and consequently bring a dramatic increase in REE extractability from  $\text{Na}_2\text{CO}_3$  sintering.

We have reported an anomalous enrichment of REE, Ga and Nb in the tuff associated with the late Permian coal-bearing strata in the Zhongliangshan mine, Chongqing, southwestern China, which can be regarded as a potential economically significant coal-bearing strata hosting a polymetallic ore deposit [18]. In order to gain more insights on the modes of occurrence of these metals and further provide a reliable basis for future industrial production, this work expanded the previous findings and investigated the extractability of REE, Ga and Nb in the tuff subjected to a sequential alkaline sintering-water immersion-acid leaching process. A tentative test was conducted at first so as to primarily see the results and optimize the extraction conditions. In this work, we designed a three-step extraction experiment with a combination of alkaline sintering, water immersion and acid leaching to investigate the extractability of REE, Ga and Nb in the tuff samples examined. Subsequently, to validate the experimental procedures as well as the optimized conditions, the whole extraction process was performed again on the tuff sample under the optimum conditions. The results can be used to identify the validity of the adopted extraction strategy and gauge the accessibility of these rare metals in the tuff through chemical processes.

## 2. Materials and Methods

### 2.1. Materials

The tuff samples used in this work were collected from the bottom layer of the Longtan Formation in the late Permian coal-bearing strata in the Zhongliangshan mine, Chongqing, southwestern China. The major elements and selected rare metal concentrations of the tentative and validation experimental samples, named as T-1, Y-1, respectively, are tabulated (Table 1). According to the study by Zou et al. [18], the mineralogical composition of the tuff includes mainly kaolinite, illite, pyrite, anatase, calcite, gypsum, quartz, and traces of zircon, florencite, jarosite, and barite.

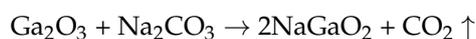
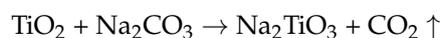
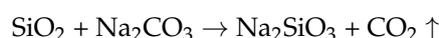
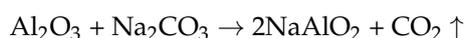
**Table 1.** Major elemental concentrations of experimental samples (%).

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
T-1	35.69	29.84	9.43	0.2	0.13	0.12	0.12
Y-1	37.53	31.88	6.89	0.2	0.12	0.13	0.17
SD	0.92	1.02	1.27	0	0.005	0.005	0.025
Sample	MnO	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	REE (μg/g)	Ga (μg/g)	Nb (μg/g)	
T-1	0.023	2.58	0.062	1515	77	215	
Y-1	0.01	2.97	0.051	1585	86	225	
SD	0.009	0.276	0.008	49.5	6.36	7.07	

Note: Rare earth elements (REE) include lanthanides and Yttrium; SD: Standard Deviation.

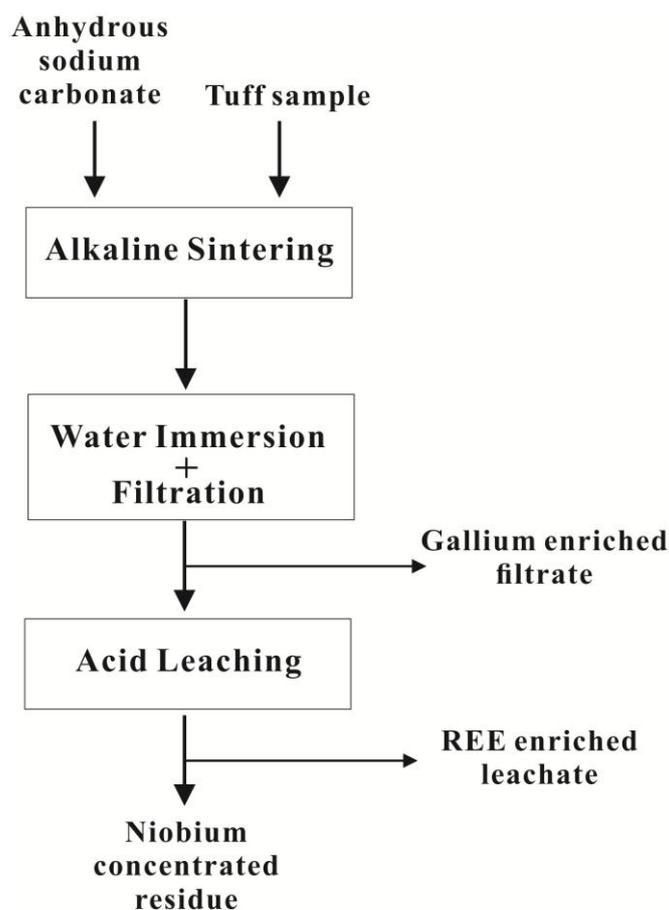
### 2.2. Experimental Procedure

The procedure of the alkaline sintering-water immersion-acid leaching method (ASWIAL) is illustrated in Figure 1, consisting principally of three steps. Firstly, the REE-, Ga-, and Nb-bearing minerals in the tuff sample are decomposed by reacting with anhydrous sodium carbonate, and converted into water soluble or metallic acid compounds through the process of alkaline sintering under high-temperature calcining. Secondly, the soluble components in the post-calcination material are leached out by immersing in hot water and are concentrated in the filtrate after filtration. Finally, the filtration residue after water immersion is leached using hydrochloric acid, and the acid-leaching residue is reserved. All liquid and solid products during this process were collected for later elemental determinations. Chemical reactions involved in the alkali sintering process are listed below:



### 2.3. Analytical Method

Concentrations of major element oxides including SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, MnO, TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> in the tuff samples were determined by X-ray fluorescence spectrometry (PANalytical Axios pw4400, PANalytical, Almelo, The Netherlands). The contents of trace elements including REE, Ga and Nb were determined by inductively coupled plasma mass spectrometry (Thermo X series II ICP-MS, ThermoFisher Scientific, Waltham, MA, USA). The detailed experimental procedures of ICP-MS analysis have been described by Zou et al. [18]. The X-ray diffraction (XRD) analysis was conducted using a D8 advance powder diffractometer with Ni-filtered Cu-Kα radiation and a scintillation detector (Bruker Corporation, Billerica, MA, USA). The XRD pattern was recorded over a 2θ interval of 2.6°–70°, with a step size of 0.02°.



**Figure 1.** The schematic diagram of the alkaline sintering-water immersion-acid leaching process.

### 3. Results and Discussion

#### 3.1. Tentative Experiment

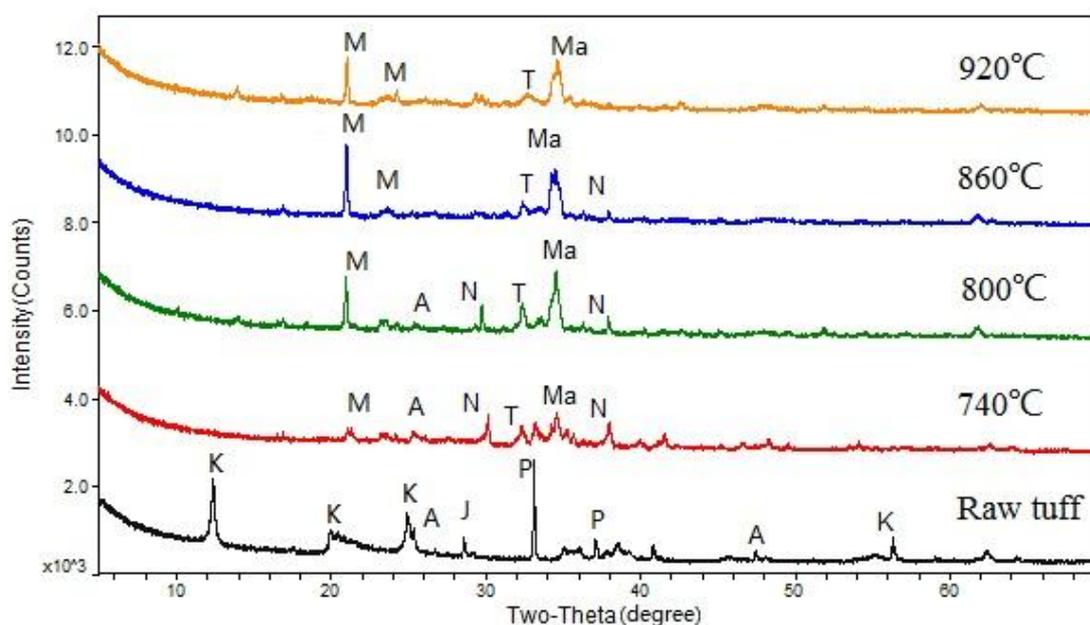
##### 3.1.1. Alkaline Sintering

The sample (T-1) used in the tentative experiment was oven-dried at 105 °C for 2 h, and ground in an agate mill (GSXX-4) at 300 r/min for 30 min. Pulverized samples were examined using a Malvern Laser Particle Sizer (MS2000 type, Malvern Instruments Ltd., Malvern, UK) to ensure that the average particle size was lower than 46 μm.

The most abundant element oxides of the tuff sample are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> [18]. The mass ratio of the sample versus anhydrous sodium carbonate was determined as 1:1.5 according to the chemical reaction equation of Si, Al and Ti with anhydrous sodium carbonate. Considering the great influence of the calcination temperature on the decomposition of minerals and the liberation of rare metal elements, the samples were tentatively calcined at 740 °C, 800 °C, 860 °C and 920 °C, respectively. The resulting solids of calcination were cooled and further subjected to XRD analysis for mineralogical identification.

The tuff sample is mainly characterized by kaolinite, pyrite, anatase and jarosite in mineralogical compositions [18]. As can be deduced from Figure 2, kaolinite, pyrite and jarosite were decomposed at 740 °C, whereas the primary representative peak of anatase at approximately 25.3° 2-Theta was still obvious, thereby indicating that the anatase was not decomposed at this temperature as well as at 800 °C. As the calcination temperature increased, anatase started to decompose, which was evidenced by the disappearance of anatase peaks at 860 °C and 900 °C. Therefore, the calcination temperature

860 °C was recommended for later experiment. Since no significant difference was observed between calcination times of 0.5 h and 1 h, 0.5 h was adopted.



**Figure 2.** X-ray diffraction spectra of calcined tuff samples at different temperatures. (K: kaolinite; A: anatase; P: pyrite; J: jarosite; M: microcline; Ma: magnesian carpholite; N: natrite; T: thermonatrite).

### 3.1.2. Water Immersion

Before water immersion, the sintering products were ground and stirred. The post-sintering products were immersed in hot water at 90 °C, where soluble components such as Ga- and Al-bearing compounds were able to be separated from the solid matrix into the liquid phase. The concentration of rare metals including REE, Ga and Nb in the filtrate and residue were determined by ICP-MS and the leaching efficiency was further calculated. The filtration residues after water immersion were subjected to the following acid leaching process.

Nine groups of samples were prepared in parallel for the water immersion. Accurately-weighed 10 g samples were mixed with 15 g of anhydrous sodium carbonate and then stirred carefully to reach a visually homogeneous color. The mixture was then fully calcined at 860 °C for 0.5 h. Each of the resultant nine post-calcined products were cooled to ambient temperature prior to being immersed using 150 mL ultrapure water at 90 °C for 2 h.

The water immersion extraction efficiency was calculated by the equation as follows:

$$\beta = \left( 1 - \frac{m_1 \times \varepsilon_1}{m_0 \times \varepsilon_0} \right) \times 100\% \quad (1)$$

where  $\beta$  is the water immersion extraction efficiency, %;  $m_0$  is the weight of the tuff sample, g;  $\varepsilon_0$  is the weight fraction of REE, Ga, Nb or Al of the tuff sample, %;  $m_1$  is the weight of the water immersion residue, g; and  $\varepsilon_1$  is the REE, Ga, Nb or Al weight fraction of the water immersion residue, %.

As indicated by the results listed in Table 2, hot water can leach most of Ga and a portion of Al from the sample. The immersion extraction efficiency of Ga varies from 54.97% to 71.11% among the nine groups, with an average of 64.55%. The Al immersion extraction efficiency is from 39.19% to 44.53% and averages at 41.98%. Although hot water is incapable of leaching REE and Nb out, with the immersion extraction efficiencies of REE and Nb being both below than 0.03%, Ga can be separated from Si, Fe and REE, which provides a basis for the further purification of Ga.

**Table 2.** Water immersion extraction efficiency (%) of elements of interest.

Sample No.	Al	Ga	Nb	REE
1	43.13	63.67	0.03	0.03
2	42.77	66.97	0.02	0.02
3	42.92	70.65	0.02	0.03
4	44.53	60.82	0.02	0.02
5	42.92	71.11	0.01	0.01
6	39.18	64.98	0.01	0.01
7	41.07	68.85	0.01	0.01
8	40.48	54.97	0.01	0.01
9	40.83	58.93	0.01	0.01
Average	41.98	64.55	0.02	0.02
Standard Deviation	1.58	5.19	0.01	0.01

### 3.1.3. Acid Leaching

The leaching experiment using hydrochloric acid as a lixiviant was carried out to extract the target metals from the water immersion residue. An orthogonal array of  $L_9(3^4)$ , which denotes four factors at three levels, was designed in consideration of the major factors relevant to the leaching process including: liquid to solid ratio, leaching temperature, leaching time, and acid concentration, which are represented by A, B, C, and D, respectively (Table 3).

The acid leaching ratio was calculated by the equation as follows:

$$\alpha = \left( 1 - \frac{m_2 \times \varepsilon_2}{m_1 \times \varepsilon_1} \right) \times 100\% \quad (2)$$

where  $\alpha$  is the acid leaching ratio, %;  $m_1$  is the weight of the water immersion residue, g;  $\varepsilon_1$  is the weight fraction of REE, Ga or Nb of the water immersion residue, %;  $m_2$  is the weight of the acid leaching residue, g; and  $\varepsilon_2$  is the REE, Ga or Nb weight fraction of the acid leaching residue, %.

**Table 3.** Acid leaching factors.

Level	A	B/ $^{\circ}$ C	C/h	D/mol/L
1	20 mL:1 g	40	2	4
2	30 mL:1 g	60	4	6
3	40 mL:1 g	80	6	8

The results of the range analysis are tabulated in Tables 4 and 5. As indicated by the results, the most influential factor on the leaching efficiency of REE and Ga is the liquid to solid ratio, followed by leaching time, leaching temperature and HCl concentration.

**Table 4.**  $L_9(3^4)$  Orthogonal array design and acid leaching results of REE (%).

Sample No.	Factors				Leaching Efficiency
	A	B	C	D	
1	1	1	1	1	85.56
2	1	2	2	2	84.97
3	1	3	3	3	83.65
4	2	1	2	3	71.82
5	2	2	3	1	79.82
6	2	3	1	2	80.71
7	3	1	3	2	81.79
8	3	2	1	3	84.59
9	3	3	2	1	80.85

Table 4. Cont.

Sample No.	Factors				Leaching Efficiency
	A	B	C	D	
I <sub>j</sub>	254.18	239.17	250.86	246.23	
II <sub>j</sub>	232.35	249.38	237.64	247.47	
III <sub>j</sub>	247.23	245.21	245.26	240.06	
K <sub>j</sub>	3	3	3	3	
I <sub>j</sub> /K <sub>j</sub>	84.73	79.72	83.62	82.08	
II <sub>j</sub> /K <sub>j</sub>	77.45	83.13	79.21	82.49	
III <sub>j</sub> /K <sub>j</sub>	82.41	81.74	81.75	80.02	
D <sub>j</sub>	7.28	3.40	4.41	2.47	

Note: j: the column of A, B, C and D; I<sub>j</sub>: the sum of leaching efficiency in the first level and j column; II<sub>j</sub>: the sum of leaching efficiency in the second level and j column; III<sub>j</sub>: the sum of leaching efficiency in the third level and j column; K<sub>j</sub>: the number of the same level in column j; I<sub>j</sub>/K<sub>j</sub>: the average of leaching efficiency in the first level and j column; II<sub>j</sub>/K<sub>j</sub>: the average of leaching efficiency in the second level and j column; III<sub>j</sub>/K<sub>j</sub>: the average of leaching efficiency in the third level and j column; D<sub>j</sub>: range value in the j column,  $D_j = \max\{I_j/K_j, II_j/K_j, III_j/K_j\} - \min\{I_j/K_j, II_j/K_j, III_j/K_j\}$ .

Table 5. L<sub>9</sub>(3<sup>4</sup>) Orthogonal experiment design and acid leaching efficiencies of Ga (%).

Sample No.	Factors				Leaching Efficiency (%)
	A	B	C	D	
1	1	1	1	1	83.48
2	1	2	2	2	84.62
3	1	3	3	3	80.94
4	2	1	2	3	77.11
5	2	2	3	1	78.57
6	2	3	1	2	80.42
7	3	1	3	2	82.59
8	3	2	1	3	87.12
9	3	3	2	1	77.38
I <sub>j</sub>	249.04	243.18	251.02	239.43	
II <sub>j</sub>	236.10	250.31	239.11	247.63	
III <sub>j</sub>	247.09	238.74	242.10	245.17	
K <sub>j</sub>	3	3	3	3	
I <sub>j</sub> /K <sub>j</sub>	83.01	81.06	83.67	79.81	
II <sub>j</sub> /K <sub>j</sub>	78.70	83.44	79.70	82.54	
III <sub>j</sub> /K <sub>j</sub>	82.36	79.58	80.70	81.72	
D <sub>j</sub>	4.31	3.86	3.97	2.73	

Note: the meaning of I<sub>j</sub>, II<sub>j</sub>, III<sub>j</sub>, K<sub>j</sub>, I<sub>j</sub>/K<sub>j</sub>, II<sub>j</sub>/K<sub>j</sub>, III<sub>j</sub>/K<sub>j</sub>, D<sub>j</sub> is the same as Table 4.

It is clear that A1B2C1D2 is the optimum with respect to the total leaching of REE and Ga. However, the leaching efficiencies of REE and Ga in A1B1C1D1 are similar to that in A1B2C1D2. Moreover, if this experiment is applied to industrial production, the cost of the A1B1C1D1 is cheaper than the A1B2C1D2, so A1B1C1D1 offers comparatively optimum conditions for acid leaching, namely the liquid-solid ratio of 20:1 (mL:g), leaching time of 2 h, leaching temperature of 40 °C and hydrochloric concentration of 4 mol/L. The leaching efficiencies of REE and Ga reached 85.56% and 83.48%, respectively, under these conditions. However, the leaching efficiency of Nb is only 3.2% (Table 6), suggesting the significant concentration of Nb in the leaching residue, which needs to be further extracted.

**Table 6.**  $L_9(3^4)$  Orthogonal experiment design and acid leaching efficiencies of Nb (%).

Sample No.	Factors				Leaching Efficiency (%)
	A	B	C	D	
1	1	1	1	1	3.2
2	1	2	2	2	1.01
3	1	3	3	3	2.46
4	2	1	2	3	6.87
5	2	2	3	1	1.36
6	2	3	1	2	2.88
7	3	1	3	2	3.32
8	3	2	1	3	11.02
9	3	3	2	1	1.74
$I_j$	6.67	13.39	17.10	6.30	
$II_j$	11.11	13.39	9.62	7.21	
$III_j$	16.08	7.08	7.14	20.35	
$K_j$	3	3	3	3	
$I_j/K_j$	2.22	4.46	5.70	2.10	
$II_j/K_j$	3.70	4.46	3.21	2.40	
$III_j/K_j$	5.36	2.36	2.38	6.78	
$D_j$	3.14	2.10	3.32	4.68	

Note: the meaning of  $I_j$ ,  $II_j$ ,  $III_j$ ,  $K_j$ ,  $I_j/K_j$ ,  $II_j/K_j$ ,  $III_j/K_j$ ,  $D_j$  is the same as Table 4.

### 3.2. Validation Experiment

To test the reproducibility of the results obtained from the tentative experiment under the optimized conditions, a duplicate tuff sample (Y-1) was subjected to the leaching procedure. The validation experiment was conducted under the optimum conditions for the ASWIAL process, listed as follows: calcining at 860 °C for 0.5 h with a sample to sintering agent ratio of 1:1.5, immersing at 90 °C for 2 h with 150 mL hot water, and leaching by 4 mol/L HCl at 40 °C for 2 h with a liquid-solid ratio of 20:1 (mL:g). It can be seen from Table 7 that the validation experiment basically produced similar results to those obtained from the tentative experiment. The water immersion efficiency and acid leaching efficiency of Ga were 67.31% and 79.71%, respectively, and the total leaching efficiency was up to 93.37%. The REE water immersion efficiency was less than 1%, and acid leaching and total leaching efficiency were both 85.81%. Nb was barely leached out during the process, but was greatly concentrated in the residue (the concentration of Nb in the acid leaching residue was up to 338 µg/g), which needs to be further extracted.

**Table 7.** Leaching efficiency of verifying sample (%).

Experiment Step	REE	Ga	Nb
Water immersion	<0.4	67.31	<1
Acid leaching	85.81	79.71	<1
Total leaching	85.81	93.37	<1

## 4. Conclusions

Rare earth elements, gallium and niobium enriched in the tuff of a coal-bearing strata-hosted rare metal deposit in the Zhongliangshan mine, Chongqing, China, can be effectively extracted using the method of alkaline sintering-water immersion-acid leaching (ASWIAL). According to the results of the tentative experiment, the optimum conditions for the ASWIAL process are calcining at 860 °C for 0.5 h with a sample to sintering agent ratio of 1:1.5, immersing at 90 °C for 2 h with 150 mL hot water, and leaching by 4 mol/L HCl at 40 °C for 2 h with a liquid-solid ratio of 20:1 (mL:g). The total leaching efficiencies of Ga and REE can be up to 93.37% and 85.81%, respectively. However, Nb is barely leached out through the process (<1%), which needs further extraction.

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**Author Contributions:** Jianhua Zou and Heming Tian collected tuff samples in Zhongliangshan mine. Jianhua Zou was responsible for the experimental design. Heming Tian and Zhen Wang were responsible for the water leaching and acid leaching experiments. All the authors were responsible for the manuscript preparation.

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

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