# EXPERIMENTAL ARTICLES

# Leaching of Rare Earth Elements from Coal Ashes Using Acidophilic Chemolithotrophic Microbial Communities

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**Abstract**—A method for leaching rare earth elements from coal ash in the presence of elemental sulfur-oxidizing communities of acidophilic chemolithotrophic microorganisms was proposed. The optimal parameters determined for rare element leaching in reactors were as follows: temperature, 45°C; initial pH, 2.0; pulp density, 10%; and the coal ash to elemental sulfur ratio, 10: 1. After ten days of leaching, 52.0, 52.6, and 59.5% of scandium, yttrium, and lanthanum, respectively, were recovered.

Keywords: coal ashes, acidophilic chemolithotrophic microbial communities, elemental sulfur, physico-chemical parameters, rare earth metals

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Production of rare metals (RM), including light metals, refractory, scattered, rare earth, and radioactive elements, is of crucial importance for development of many fields of industry, such as electronics, nuclear power engineering, mechanical engineering, and production of special alloys. The group of rare earth metals (REM), such as scandium, yttrium, lanthanum, cerium, ytterbium, neodymium, etc., is of special importance. REM are in short supply worldwide, which results in increasing prices. The search for new REM sources and technologies for their recovery is therefore of high priority.

Thermal treatment of coal (burning, gasification, or chemical processing) produces solid (ash and slag) and gaseous waste. Accumulation of ash and slag in waste piles may cause contamination of air and soil due to dust rising, as well as contamination of water due to erosion by rains, melted snow, or flood water [1-3]. Worldwide, over  $700 \times 10^6$  t of ash—slag waste (ASW) is produced yearly.

Importantly, ASW are technogenic concentrates accumulating various chemical elements, including rare metals. In Russia, ASW utilization does not exceed 4–5% which is much less than in developed countries (50, 70, and up to 90% for Europe on average, France and Germany, and Finland, respectively) [4].

A number of technical solutions exists for ASW utilization as supplements for construction materials, such as concrete or wall panels, as components of ferrosilicon slag in metallurgy, as agricultural microfertilizers, etc.

In some developed countries, such as United States, state programs for industrial production of rare metals from new sources are developed and implemented. Some of these metals are thus processed from ASW of thermal power plants, rather than from natural ores [5-10].

All traditional technologies for recovery of rare and rare earth metals include two steps: leaching from raw material as a collective product (as a rule, acidic and alkaline leaching is used) and subsequent separation (solvent extraction, sorption, and precipitation as sulfides or ammonium complexes). Existing technologies make it possible to achieve high degrees of recovery of valuable components. Thus, up to 57% of REM (50 mg/dm³) may be recovered from acidic solutions (pH 0.5–2.5) with high contents of iron and aluminum (1 g/L) by using a microporous sulfonic cation exchange resin based on super-cross-linked polystyrene [11].

These technologies for ASW leaching have, however, several shortcomings. Most authors recommend leaching with concentrated acid solutions at high temperatures, which requires high power inputs and may be environmentally hazardous.

Since ASW has low content of valuable metals, approaches are required which decrease investments and operating costs. Heap bioleaching by acidophilic chemolithotrophic iron- and sulfur-oxidizing microorganisms is a successful technology for metal recovery from low-grade sulfide ores. It was calculated that this approach requires lower expenditure for recovery of nonferrous metals from poor sources than other known technologies [12]. This technology was developed for metal recovery from sulfide materials, which are used by acidophilic chemolithotrophic microor-

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ganisms as energy sources, and is presently broadly used worldwide [13].

Unlike sulfide ores, ASW does not contain components which may be used as energy substrates by microorganisms. However, application of microbial biotechnologies for ASW processing is possible if a cheap substrate is provided for microbial oxidation, which will result in the acid formation and pH decrease required for metal leaching. Elemental sulfur produced in the course of oil and gas purification from sulfurous contamination is one of readily available substrates.

It was previously shown that elemental sulfur was a better energy substrate than thiosulfate or tetrathionate for decreasing pH of the culture liquid by indigenous and experimentally constructed microbial community [14]. Sulfur oxidation at 28°C by an experimentally constructed microbial community resulted in lower pH (0.75) than the same process carried out by the indigenous community isolated from an industrial bioreactor oxidizing sulfide concentrates (0.98). In the course of elemental sulfur oxidation, the strains Acidithiobacillus ferrooxidans TFO, A. thiooxidans Ol-8, A. caldus OP-1, and Sulfobacillus thermosulfidooxidans HT-3 decreased the pH of the culture liquid more rapidly than other studied *Acidithiobacil*lus and Sulfobacillus strains. Adaptation to elemental sulfur of the microbial community based on the experimentally constructed microbial community and the strains listed above under two temperature modes (28) and 45°C) resulted in pH decreasing to 0.7 and 0.9. respectively, after six days of cultivation.

The goal of the present work was to investigate the possibility of leaching rare earth metals from ash—slag waste by acidophilic chemolithotrophic microbial communities in the presence of elemental sulfur.

## MATERIALS AND METHODS

The subjects of study were: ash—slag material from heaps of Kashira heat power station, Dzerzhinskii, Russia, and two communities of acidophilic chemolithotrophs adapted to elemental sulfur at 28 and 45°C [14].

Physical, chemical, and mineralogical properties of ASW were analyzed using the following methods: mass spectral analysis with inductively coupled plasma on Elan-6100 mass spectrometer (Perkin Elmer, United States) and atomic emission analysis with inductively coupled plasma on an Optima-4300 DV spectrometer (Perkin Elmer, United States). Phase composition was studied by X-ray phase analysis on an X-Pert PRO X-ray diffractometer (Panalytical, The Netherlands). Chemical composition was determined using a MagiX PRO X-ray fluorescence spectrometer (Panalytical, The Netherlands).

The pH of the culture liquid was measured with an Ekspert-001 pH-meter—ion meter (Ekoniks-Ekspert, Russia). Cell numbers were determined by direct cell

count in an Amplival phase contrast microscope (Carl Zeiss, GDR).

**Percolator experiments.** Laboratory percolators (300 mL) were loaded with homogenously mixed ash—slag material (220 g) and elemental sulfur (8 g). Non-acidified salt solution of 9K mineral medium without ferrous sulfate [15] (100 mL) was added to each percolator. Of this amount, 86 mL was used for ASW moistening. Moisture capacity of ASW was therefore 37.7%. Each percolator was then inoculated with 100 mL of the culture of a mesophilic chemolithotrophic acidophilic microbial community with pH 0.8 and  $7 \times 10^8$  cells/mL [14]. The temperature of the process was maintained at  $20-22^{\circ}$ C, aeration rate was 5 L/min.

Prior to inoculation, ASW was treated with sulfuric acid to adjust pH to 1.6. This required  $41 \pm 1 \text{ kg/t}$   $H_2SO_4$ .

**Experiments in laboratory reactors.** ASW processing was carried out in batch mode in 2.5-L reactors with turbine stirrers (500 rpm), Hiblow HP-20 compressors (HIBLOW Techno Takatsuki, Japan) for aeration (4 L/min), and ED thermostats (Julabo, Germany) for maintaining the operating temperature at  $28 \pm 1$  or  $45 \pm 1^{\circ}$ C.

Prior to inoculation, ASW was treated with sulfuric acid to adjust the pH to 2.0. This required  $45 \pm 1$  kg/t  $H_2SO_4$ .

#### RESULTS AND DISCUSSION

Physicochemical and mineralogical properties of ASW. Chemical and mineralogical analysis of ash—slag material from the heaps of Kashira heat power station, Dzerzhinskii, Russia, was carried out. The studied ASW samples were found to contain relatively low amounts of rare earth metals (g/t): cerium (80.0), lanthanum (46.0), neodymium (39.0), yttrium (31.0), praseodymium (10.0), scandium (9.4), samarium (7.2), gadolinium (6.5), dysprosium (5.7), erbium (3.6), and europium (1.2). Investigation of phase composition revealed quartz (7%), mullite (7%), hematite (2.5%), magnetite (2%), and calcite (1%).

Leaching of rare earth minerals in percolators. The mesophilic acidophilic chemolithotrophic microbial community with a high rate of sulfur oxidation was used for experiments on leaching of rare earth elements from ASW in airlift percolators (a laboratory analogue of heap and underground leaching) [14]. Leaching commenced after filling of the percolators. On day 5, pH increased to 7.5 due to dissolution of the carbonates and oxide minerals of the ASW. At the beginning of the process, the rate of H<sub>2</sub>SO<sub>4</sub> production by microorganisms was insufficient to maintain low pH. Since neutral pH is unfavorable for both growth of acidophilic microorganisms and metal leaching, pH not exceeding 4.0 was maintained by addition of sulfuric acid. Consumption of sulfuric acid during 60 days of the process was 9 kg/t. After 18 days, no additional

**Table 1.** Leaching of rare earth elements from ASW in percolators after 60 days

Metal	Leaching, %
Yttrium	31
Scandium	30
Lanthanum	33

acid was required, since sulfuric acid produced by microorganisms in the course of sulfur oxidation was sufficient to maintain required low pH. However, pH never decreased below 2.5 due to neutralization of the acid in the course of dissolution of oxide and carbonate minerals. At days 45–60, no significant changes in pH were observed.

At the onset of the process, the number of inoculated microorganisms was  $7 \times 10^8$  cells/mL. It did not change significantly in the course of 60-day cultivation, varying from 5 to  $9 \times 10^8$  cells/mL, in spite of sorption of microbial cells on sulfur and ASW particles. Leaching was stopped after 60 days, and the solid phase was collected for determination of metal content. The leached residue was washed with  $H_2SO_4$  solution (pH 1.5), then with distilled water, and dried. The residue yield was 98%. Results of analysis of the content of rare earth elements after 60 days of the process were used to calculate the degree of their leaching (Table 1).

Scandium (30%), yttrium (31%), and lanthanum (33%) were leached from ASW.

Effect of the Major Physicochemical Parameters of the Pulp on Leaching of Rare Earth Elements from ASW in Reactors

Leaching of rare earth elements at different temperatures. Temperature has a major effect on the rate of chemical reactions. Under different temperature modes, specific acidophilic chemolithotrophic microbial communities develop, usually with predominance of the species with the temperature optimum close to the process temperature. The oxidative activity of various microbial species and their communities may vary considerably. Effect of temperature on dynamics of rare earth element leaching from ASW was therefore studied. Three cultivation temperatures were studied: 28°C (optimum for the mesophilic species A. ferrooxidans and A. thiooxidans), 40°C (optimum for some Sulfobacillus species), and 45°C (optimum for moderately thermophilic A. caldus and some Sulfobacillus species).

For leaching of rare earth elements from ASW at 28°C, a mesophilic community of acidophilic chemolithotrophic microorganisms was used as inoculum, while a moderately thermophilic acidophilic chemolithotrophic community was used as inocula for the processes conducted at 40 and 45°C [14]. Pulp density was 10%, while the ratio of ASW to elemental sulfur was 10:1.

Physicochemical parameters of the pulp liquid phase during ASW bioleaching at different temperatures are presented in Table 2. The highest rate of pH decrease, implying the highest rate of S<sup>0</sup> oxidation, was observed at 45°C. In this case, after 10 days of bioleaching pH was 1.15, while at 28 and 40°C pH values were 1.41 and 1.27, respectively. At 45°C, the

**Table 2.** Physicochemical parameters of the pulp liquid phase in the course of ASW bioleaching in reactors at different temperatures

	Temperature, °C									
T: 1		28			40			45		
Time, days	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	
0	1.60	690	0.7	1.60	690	0.7	1.60	690	0.7	
1	1.78	675	0.6	1.73	678	1.0	1.63	681	3.1	
2	1.70	668	1.4	1.70	691	1.5	1.50	732	3.0	
3	1.68	665	1.6	1.64	700	3.4	1.44	740	4.6	
4	1.67	666	2.1	1.62	709	4.2	1.38	768	7.1	
5	1.60	668	3.0	1.58	718	4.5	1.35	776	7.0	
6	1.55	668	4.5	1.51	725	4.5	1.32	789	6.5	
7	1.52	669	5.0	1.45	728	4.8	1.29	803	6.3	
8	1.49	664	5.0	1.39	741	5.2	1.26	809	6.5	
9	1.46	659	4.9	1.34	750	5.0	1.20	804	6.0	
10	1.41	676	4.8	1.27	759	5.0	1.15	817	5.6	

Metal		Content, µg/g		Recovery, %			
	28°C	40°C	45°C	28°C	40°C	45°C	
Cobalt	14.0	14.0	14.0	13.2	12.3	16.0	
Nickel	35.0	32.0	31.0	37.4	42.2	46.3	
Copper	39.0	39.0	36.0	39.6	38.9	46.0	
Zinc	50.0	62.0	48.0	61.3	51.4	64.0	
Scandium	8.8	8.7	7.4	12.9	13.0	29.1	
Yttrium	28.0	26.0	25.0	16.0	21.2	27.4	
Lanthanum	42.0	39.0	35.0	15.1	20.3	31.5	
Neodymium	39.0	38.0	38.0	7.0	8.4	12.3	
Samarium	6.9	6.9	7.0	10.9	9.9	12.5	
Gadolinium	6.0	6.2	6.1	14.2	10.3	15.5	

**Table 3.** Trace contaminant composition of ASW bioleached residues and the degree of solubilization of the elements at different temperatures in reactors

**Table 4.** Chemical composition of ASW bioleached residues (as oxides) in reactors at different temperatures

Metal	Symbol	Content in original	Content, %				
	Symbol	ASW, %	28°C	40°C	45°C		
Sodium	Na <sub>2</sub> O	0.50	0.47	0.51	0.48		
Magnesium	MgO	0.80	0.75	0.69	0.77		
Aluminum	$Al_2O_3$	17.80	21.0	21.0	21.0		
Potassium	K <sub>2</sub> O	1.60	1.80	1.90	1.90		
Calcium	CaO	1.30	0.75	0.82	0.75		
Titanium	TiO <sub>2</sub>	0.70	0.66	0.69	0.68		
Manganese	MnO	0.10	0.14	0.15	0.15		
Iron	Fe <sub>2</sub> O <sub>3</sub>	6.0	8.30	8.70	8.70		

number of microbial cells in the pulp was higher, as well as the redox potential, which exceeded 800 mV by the end of the process.

The trace contaminant composition of ASW bioleached residues and the degrees of solubilization of the elements at different temperatures are listed in Table 3. Increased temperature of the process resulted in decreased content of rare earth elements and thus in their better solubilization. Temperature had the most pronounced effect on bioleaching of scandium, yttrium, and lanthanum. Increase in temperature from 28 to 45°C resulted in their leaching increase 2.2-, 1.7-, and 2.1-fold, respectively.

Table 4 presents the major chemical composition of ASW bioleached residues at different temperatures. It may be seen that bioleaching of rare earth elements did not cause considerable changes in the major slag components (aluminum silicates, mica, quartz, etc.).

Thus, bioleaching of rare earth elements from ASW at 45°C provided the best results, with more intense S<sup>0</sup>

oxidation in the pulp and therefore more rapid pH decrease and better solubilization of rare earth elements (scandium, yttrium, and lanthanum).

All subsequent experiments on the technological modes of bioleaching of rare earth elements from ASW were carried out at 45°C.

Leaching of rare earth elements at different pH values. The pH value is the key parameter for leaching of sulfide materials and man-made wastes by acidophilic chemolithotrophic microorganisms. Hydrogen ions are the main agent involved in leaching rare earth elements from ASW. High H<sup>+</sup> concentrations, however, inhibit activity of chemolithotrophic acidophilic microorganisms, with the inhibiting concentration depending on the species. Determination of the optimal pH of the pulp is therefore essential for investigation of the processes of bioleaching of rare earth elements from various sources, including ASW.

	Initial pH									
Time, days		3.0			2.6			2.0		
	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	
0	3.0	659	0.7	2.60	679	0.7	2.00	673	0.7	
1	1.95	756	0.6	1.90	752	0.6	1.80	742	0.5	
2	1.48	789	2.5	1.50	790	3.0	1.34	785	2.0	
3	1.23	825	7.4	1.23	798	8.2	1.14	820	5.9	
4	1.15	831	10.0	1.15	805	9.9	1.09	833	8.4	
5	1.08	845	8.5	1.08	821	9.1	1.04	841	9.5	
6	1.03	850	7.6	1.02	843	9.1	1.00	852	9.0	
7	0.98	852	6.4	0.98	856	8.7	0.98	853	8.2	
8	0.95	846	6.4	0.94	850	7.1	0.95	855	8.5	

0.92

0.90

850

846

7.5

7.0

**Table 5.** Physicochemical parameters of the pulp liquid phase in the course of ASW bioleaching in reactors at different initial pH values

Pulp density in the experiments was 10%, ASW to  $S^0$  ratio was 10:1.

845

845

6.0

6.0

0.94

0.92

9

10

Initial pH values were adjusted to 3.0, 2.6, or 2.0 by addition of concentrated sulfuric acid.  $H_2SO_4$  consumption was  $21 \pm 3$  kg/t for initial pH 3.0 and 2.6 and  $45 \pm 1$  kg/t for pH 2.0.

The physicochemical parameters of the pulp in the course of ASW leaching at different initial pH values are presented in Table 5. Initial pH within the 2.0-3.0 range had no effect on the sulfur-oxidizing activity of the moderately thermophilic community of acidophilic chemolithotrophic microorganisms. The highest number of microbial cells (9.5–10.0  $\times$ 108 cells/mL) was observed on days 4–5 of the process and did not change significantly depending on initial pH. The redox potential increased gradually, reaching 845–855 mV by the end of the bioleaching, which was an indication of the highest valences of the ions in the medium. At initial pH 3.0, more active H<sub>2</sub>SO<sub>4</sub> formation was observed during the first four days. Subsequently, the rates of microbial H<sub>2</sub>SO<sub>4</sub> formation were similar in all variants, with the final pH value of  $\sim 0.9$ . This was an indication of high sulfur-oxidizing activity of the moderately thermophilic community of acidophilic chemolithotrophic microorganisms.

Thus, since prolonged ASW incubation under acidic conditions favors efficient recovery of rare earth elements, initial pH 2.0 was accepted as the optimal value. All subsequent experiments on bioleaching of

rare earth elements from ASW were conducted at initial pH 2.0.

0.92

0.90

854

855

7.1

7.1

Leaching of rare earth elements at different pulp densities. The hydrodynamic conditions are an important parameter of chemical processes in a reactor. The content of the solid phase in a suspension (pulp density) is one of the major parameters affecting the hydrodynamic conditions in the reactor. In order to determine the efficiency of rare element leaching from ASW, based on the hydrodynamic conditions in the reactor, experiments were carried out at different values of pulp density. Pulp densities of 10 and 33% (wt/vol) of the solid phase in the liquid were tested. The ASW to S<sup>0</sup> ratio was 10:1.

The physicochemical parameters of the pulp liquid phase in the course of ASW bioleaching at various values of pulp density are presented in Table 6. It can be seen that pH decrease was more efficient at 10% pulp density, especially during the first six days of the process. At pulp densities of 10 and 33%, the final pH in the liquid phase was 0.90 and 1.07, respectively. At 33% pulp density, pH increased from 2.0 to 2.8 during the first day, while at 10%, pH decreased to 1.8. This was due to the chemical composition of ASW and indicated higher rates of H<sup>+</sup> consumption for neutralization at higher pulp density, exceeding the rates of acid formation by sulfur-oxidizing microorganisms.

Both at 10 and 33% pulp density, bioleaching of rare earth minerals from ASW resulted in high values of the redox potential (855 and 805 mV, respectively,

	1									
	Pulp density, %									
Time, days		10		33						
, •	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )				
0	2.0	673	0.7	2.0	673	0.7				
1	1.80	742	0.5	2.80	665	0.5				
2	1.34	785	2.0	2.10	672	2.4				
3	1.14	820	5.9	1.67	676	6.7				
4	1.09	833	8.4	1.50	683	9.4				
5	1.04	841	9.5	1.33	710	7.9				
6	1.00	852	9.0	1.22	737	8.9				
7	0.98	853	8.2	1.16	770	10.0				
8	0.95	855	8.5	1.14	781	8.5				
9	0.92	854	7.1	1.09	795	6.7				
10	0.90	855	7.1	1.07	805	6.9				

**Table 6.** Physicochemical parameters of the pulp liquid phase in the course of ASW bioleaching in reactors at different pulp densities

after ten days of incubation), indicating oxidative conditions in the pulp. In both cases, cell numbers of the moderately thermophilic acidophilic chemolithotrophic microbial community varied insignificantly, reaching  $9.5{-}10.0 \times 10^8$  cells/mL during the active growth phase.

The trace contaminant composition of ASW bioleached residues and the degrees of solubilization of the elements depending on pulp density are listed in Table 7. Pulp density had little effect on solubilization of nonferrous metals (cobalt, nickel, copper, and zinc). Increase in pulp density from 10 to 33% resulted in a drastic decrease in the rates of bioleaching of rare earth elements, including lanthanides. Thus, recovery of scandium, yttrium, and lanthanum decreased 2.72-, 1.98-, and 2.0-fold, respectively.

Table 8 presents the major chemical composition of ASW bioleached residues at different pulp densities. It may be seen that bioleaching of rare earth elements by the  $S^0$ )-oxidizing acidophilic chemolithotrophic microbial community did not cause considerable changes in the major slag components (cf. Table 4). Aluminum content decreased from 17.8 to 14.0–16.0%, while calcium content decreased from 1.3 to 0.59–0.98% due to dissolution of aluminum silicates and calcite in sulfuric acid.

Thus, among two tested pulp density values, 10% was preferable for bioleaching of rare earth elements from ASW due to more efficient S<sup>0</sup> oxidation in the pulp and therefore a more pronounced pH decrease. In this case, the highest values of scandium, yttrium, and lanthanum solubilization (52.0, 52.6, and 59.5%, respectively) were achieved.

All subsequent experiments on adjustment of the technological modes of rare earth elements leaching from ASW were carried out at 10% pulp density.

Leaching of rare earth elements at different ratios of ASW and elemental sulfur. The ratio of ASW to elemental sulfur, the substrate for sulfuric acid production by an acidophilic chemolithotrophic microbial community, is among the key parameters for leaching of rare earth elements. Low amounts of the substrate (elemental sulfur) may result in insufficient concentrations of the leaching agent in the liquid phase, while its excess may result in lower economical efficiency of bioleaching. Determination of the optimal ratio of ASW and elemental sulfur is therefore one of the most

**Table 7.** Trace contaminant composition of ASW bioleached residues and the degree of solubilization of the elements at different pulp density in reactors

Metal	Conter	nt, μg/g	Recovery, %		
Metai	10%	33%	10%	33%	
Cobalt	13.0	14.0	15.1	11.3	
Nickel	33.0	34.0	37.8	37.9	
Copper	28.0	36.0	54.3	43.0	
Zinc	59.0	54.0	51.8	57.3	
Scandium	4.6	8.0	52.0	19.1	
Yttrium	15.0	24.0	52.6	26.5	
Lanthanum	19.0	34.0	59.5	29.8	
Neodymium	31.0	38.0	22.1	7.4	
Samarium	5.4	6.7	26.5	11.6	
Gadolinium	4.8	6.0	27.6	12.3	

**Table 8.** Chemical composition of ASW bioleached residues (as oxides) in reactors at different pulp densities

Metal	Symbol	Content, %			
Metai	Symbol	10%	33%		
Sodium	Na <sub>2</sub> O	0.47	0.51		
Magnesium	MgO	0.60	0.69		
Aluminum	$Al_2O_3$	14.0	16.0		
Potassium	K <sub>2</sub> O	1.8	1.9		
Calcium	CaO	0.59	0.98		
Titanium	TiO <sub>2</sub>	0.63	0.68		
Manganese	MnO	0.12	0.15		
Iron	Fe <sub>2</sub> O <sub>3</sub>	8.0	8.4		

important stages in development of technology for bioleaching of rare earth elements. The tested ratios of ASW to elemental sulfur were 100: 1 and 10: 1.

The physicochemical parameters of the pulp liquid phase during ASW bioleaching at different ASW:  $S^0$  ratios are presented in Table 9. These results indicate a more efficient pH decrease at 10:1 ratio of ASW to elemental sulfur than at 100:1. Thus, the final pH values were 0.90 and 1.81, respectively. An increase in pH was observed during the first day of bioleaching at the 100:1 ratio between ASW and elemental sulfur.

The redox potential achieved during bioleaching at 10:1 ASW: S<sup>0</sup> ratio (855 mV) was almost 100 mV higher than at the 100:1 ratio. The number of cells in the acidophilic chemolithotrophic microbial commu-

nity was also higher in the first case  $(9.5 \times 10^8 \text{ cells/mL})$  during the active growth phase).

These data indicated that at ASW to  $S^0$  ratio of 100:1 the microbial community had insufficient energy substrate and therefore produced insufficient amounts of sulfuric acid for bioleaching of rare earth elements. In this case the concentration of the leaching agent may be insufficient for solubilization of rare earth elements.

Thus, leaching of rare earth elements from ASW provided the best results at 10 : 1 ASW to S<sup>0</sup>, under conditions characterized by a more rapid increase in the concentration of the leaching agent (hydrogen ions) in the pulp liquid phase.

Based on the results of our research on the technological parameters for recovery of rare earth elements from ASW by acidophilic chemolithotrophic microbial communities, bioleaching in reactors at 45°C, initial pH of the pulp 2.0, pulp density 10%, and 10:1 ASW to elemental sulfur ratio is recommended. Under optimal conditions, amounts of scandium, yttrium, and lanthanum recovered after ten days of bioleaching were 52.0, 52.6, and 59.5%, respectively.

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**Table 9.** Physicochemical parameters of the pulp liquid phase in the course of ASW bioleaching in reactors at different  $ASW/S^0$  ratios

Time, days		10 : 1 ratio			100 : 1 ratio	
	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )	рН	Eh, mV	cell number, cells/mL (×10 <sup>8</sup> )
0	2.0	673	0.7	2.0	673	0.7
1	1.80	742	0.5	2.09	749	0.4
2	1.34	785	2.0	2.01	774	1.0
3	1.14	820	5.9	1.95	796	5.8
4	1.09	833	8.4	1.89	800	6.5
5	1.04	841	9.5	1.84	800	6.4
6	1.0	852	9.0	1.80	798	6.5
7	0.98	853	8.2	1.78	794	6.0
8	0.95	855	8.5	1.80	782	5.0
9	0.92	854	7.1	1.80	777	3.1
10	0.90	855	7.1	1.81	766	1.9

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