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Research article

STRATEGICAL COMPOUNDS AND PRODUCTS BASED ON POOR ORES AND TAILINGS OF MANGANESE WASTE

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Abstract

Laboratory technologies for obtaining manganese from secondary resources (poor ores) of South Caucasus region (Georgia) have been developed. The process of manganese recovery from Chiatura (Georgia) poor ores and tailings have been studied. The novel bioactive coordination compounds of manganese have been synthesized. **Copyright © IJACSR, all rights reserved.**

Keywords: Manganese, poor ore, secondary resources, coordination compounds.

Introduction

Sough Caucasus region (Georgia) is rich in significant natural resources such as barite, concretes, zeolites, basalt, petroleum, manganese, copper, mercury, arsenic, gold, medical mineral waters and Black Sea reserves of hydrogen sulfide [1]. Among them manganese takes a special place [2].

Manganese remains the top- priority direction among the mineral resources of Georgia. There are several places where manganese resource was found – Chiatura, Rodinauli, Rikoti, etc. Chiatura mine is the most important among manganese deposits and is considered as one of the basic manganese-containing regions of the world.

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Extracting of ores from Chiatura deposits started from 1880 and reached to 2-3 thousands of tones in the eighties of last century. Their reserves were reduced significantly and currently extraction consists of 40-45 t/s. [3].

In spite of the aforementioned, the use of the poor ores and secondary resources and the creation of cheap materials' base increasingly acquire actuality.

Purposeful recycling of the secondary resources is performed by two main ways:

1. Recovery of manganese sulfate and metallic manganese from poor ores and tailings;
2. Use of the poor ores for creation of various complex compounds with specific properties.

They represent not only additional technical-economical reserve for any developed country but encourage solving a number of ecological problems too.

Experimental

Tests of manganese isolation were carried out in the Zestafoni plant shop (Georgia). 50 kg slime and 20 kg pyrite were used. The slime content of Mn was 13.5 %, of which 7.5 % were MnO_2, 4.7 % - $MnCO_3$ and 0.07 % - P. The slime and pyrite mixture were added with the iron-free nutrient medium 9K and the *T. ferrooxidans* strain 348, at a growing rate. Under three-day continuous agitation conditions, the solution composition was as follows: 12.2 g/L Mn; 168 g/L $(NH_4)_2SO_4$. The tests demonstrated that the solutions can be used for recovery of metallic manganese. The ore thickness was 0.15 mm; pH = 2.5; solid/liquid = 1/5; culture titer was defined – 10^8-10^9 cel/ml. The Fe^{2+} oxidation process is especially active under aeration conditions.

Results and Discussion

The objective of our study was the manganese poor ores of Georgia (Chiatura) and its tailings. At present 47 % of the Chiatura deposit is represented by poor ores of different type and its tailings being in the form of slime or dust [4].

The application of available recovery technology, consisting of the treatment of ores and tailings with the concentrated sulphuric acid is connected with the great difficulties [5]:

1. The employed concentrated sulphuric acid is rather costly and it will influence on the final product cost.
2. The presence of both liquid and solid production waste is completely inadmissible in terms of ecology. Such outdated technology is the main reason of the plants production waste that accounts for thousand of tones.

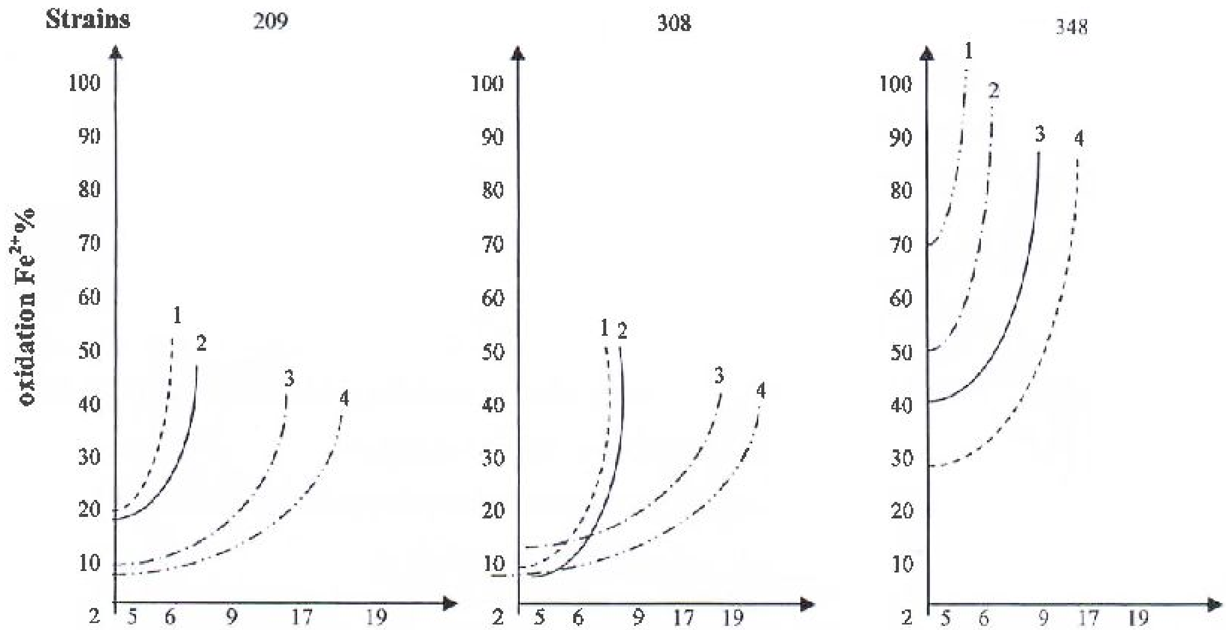
In order to shorten the length of the process of manganese recovery from the poor ores and tailings and to make it low-cost, the strain *thiobacillus ferrooxidans* and pyrite concentrate (Fe^{2+} – 57.2 %, S – 46.2 %) were used as the energy source/nutrient medium. The process is combined – *thiobacillus ferrooxidans* oxidizes pyrite by producing $FeSO_4$ and H_2SO_4 (Scheme 1a). Iron(III) sulfate hydrolysis takes place at pH = 2.5-3 by producing of iron(III) hydroxide in the residue (Scheme 1b). Concurrently, oxalic acid as bacterial metabolite is being produced (Scheme 1c). The obtained products are considered to be strong reductants of manganese(IV) oxide and solvents of manganese(II) sulfate and carbonate [8, 9]. As a result, a bivalent manganese sulfate is produced in the dissociated state (Scheme 1d, e) by the electrolysis of which metallic manganese is produced.

$$FeS_2 + 3.5O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \qquad (a)$$
$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \qquad (b)$$
$$H_2O + 2CO_2 \xrightarrow{[O]} HOOC\text{-}COOH \qquad (c)$$
$$MnO_2 + HOOC\text{-}COOH \rightarrow Mn(OH)_2 + 2CO_2 \qquad (d)$$
$$Mn(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O \qquad (e)$$

Scheme 1

The study of surrounding effects demonstrated that the process efficiently proceeded in vats under conditions of good airflow supply; the ore thickness was 0.15 mm; pH 2.5; solid/liquid - 1/5; culture titer define – 10^8-10^9 cel/ml. The Fe^{2+} oxidation process is especially active under aeration conditions (Fig. 1).

One of the principal factors of bacterial growth and intensification of its acidity function is the bacterial resistance to the sulphuric acid and heavy metal concentration in the solution.



1 - - - - - - aeration conditions 35^0C 2 ——— aeration conditions 20^0C
3 - · — · — aeration conditions 28^0C 4.._._._._.. aeration conditions 35^0C

Figure 1. Growth dynamics of the strains 209, 308 and 348 - *thiobacillus ferrooxidans* and Fe^{2+} oxidation intensity (25-35^0C); on x-axis is shown number of days

It was established that the strain 348 – *thiobacillus ferrooxidans* easily is adapted to 20-25 g/L H_2SO_4 in the solution, while during study of their physiological properties they were found to excrete oxalic acid in the solution (was established chemically as well), which is important for recovery of manganese (Table 1).

Table 1. Manganese content in starting poor ores and recovered metallic manganese using *thiobacillus ferrooxidans* strain

Ore types	**Mn content in starting ores**	**Mn content in solution, g/L**		**Mn content in solid, g/L**		**Recovered Mn, %**	
		Test	**Sample**	**Test**	**Sample**	**Test**	**Sample**
Manganese poor ore	14.75	12.3	3.4	2.45	11.3	83.6	23.3
Tailings slime	11.8	9.9	2.9	1.9	8.9	83.9	24.6
	13.62	11.8	3.6	1.8	10.1	86.6	26.2

Schematic diagram of the industrial recovery process of manganese sulfate and metallic manganese from poor ores and tailings by bacterial leaching method [6, 7] is shown on the Fig. 2.

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The advantages of elaborated method are the waste-free, environmentally sound production and the low cost of final product's (Fig. 3).

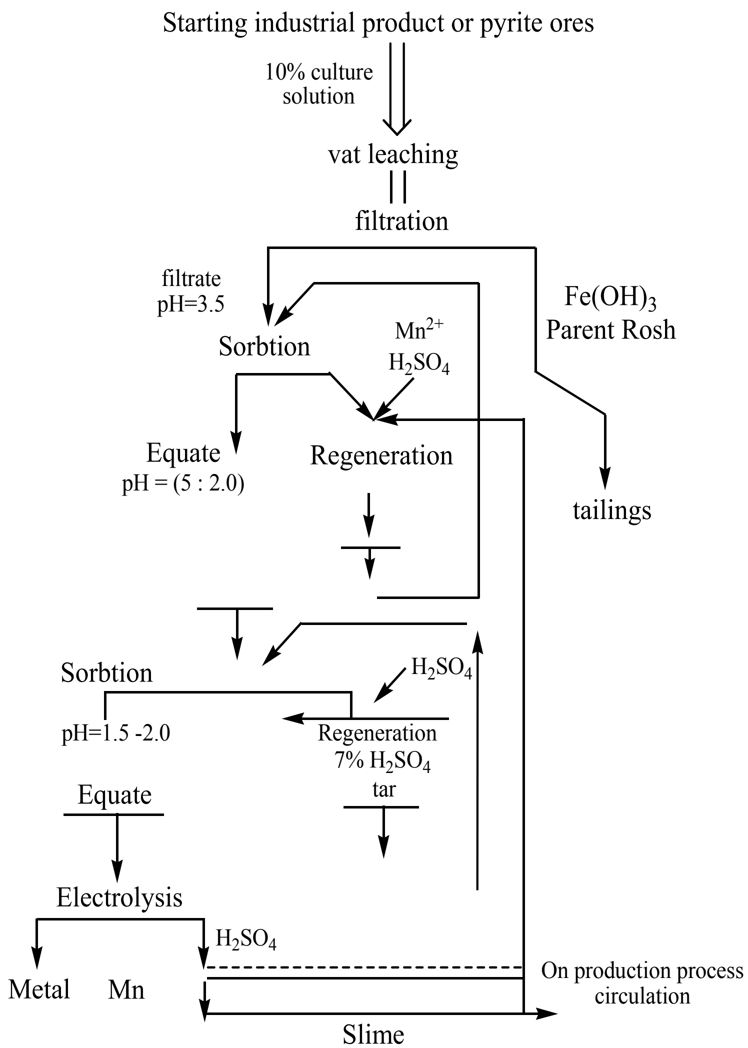
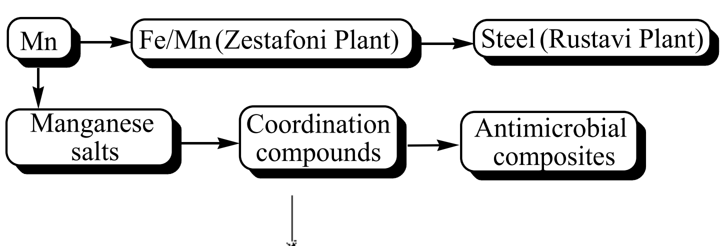


Figure 2. Schematic diagram of the industrial recovery process of manganese



$3Mn(SO_4)_2 + 3n\mathrm{dipy} + 2Na_3SbS_4{\cdot}9H_2O \rightarrow [Mn(\mathrm{dipy})_3]_3(SbS_4)_2 + 6NaX + 18H_2O$ (dipy – 2,2′-dipyridyl) [8]

Figure 3. Transformation of manganese

Thus, a method of bacterial leaching from poor balanced ores, tailings and slimes has been developed that makes it possible to recover the manganese raw material at the expense of internal resources of the production.

The said process has been patented and its copyright is reserved. The coordination compounds of manganese have been synthesized.

Conclusions

Scientific results: The laboratory technology of bacterial leaching from poor balanced ores, tailings and slimes has been developed. This makes it possible to recover the manganese raw material at the expense of internal resources of the production. Manganese coordination compounds have been synthesized.
Technical results: By using cheap base of resources new available important products have been elaborated. The possibility of their pilot survey has been considered.
Economical results: Manganese sulfate and metallic manganese from poor ore and tailings have been recovered.
Ecological Results: The compounds and multifunctional materials with specific properties by transformation of the secondary raw materials of manganese have been obtained.

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