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Characteristics and Possibilities of use of the Mining-Metallurgical Environmental Liabilities of the Refractory Chromite Mining in the Moa-Baracoa-Cuba Region

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Abstract

The old refractory chromite mines in the Moa-Baracoa region abandoned a large amount of solid mining-metallurgical environmental liabilities (PAMMs) as a result of the productive operations developed for more than 60 years. In this sense, the management of environmental affectations constitutes one of the most used measures in recent years for the rehabilitation of spaces degraded by mining in this area of the country. However, there is insufficient knowledge of the physical-chemical, mineralogical, and thermal characteristics of these residues, generated by the chrome industry in Cuba, which limits their scientific basis and the decision-making on their possible industrial uses. As a result of the research developed with these materials over more than 20 years, their refractory properties have been proved, which demonstrates the possibilities of their industrial use in metallurgical processes, and even as construction materials, which are exposed in this study.

Keywords: *Mining and Metallurgical Environmental Liabilities, Refractory Chromites.*

INTRODUCTION

In 1883, the first information about the geology of the region appeared, when the Spanish geologist B. Peletero pointed out that ultrabasic rocks were developed in the Moa region. In 1901-1905, North American geologists mentioned the presence of chromite ores in the Moa region (Pons Herrera, 2000, p. 22).

During the years 1955-1958, a North American mining company made a study of a group of deposits: Loro, Piloto, Yarey, Merceditas, and others; in the Merceditas deposit, 408 linear m (6 wells) were drilled and 7 cleanings were done (Pons Herrera et al., 2014, p. 33).

In 1962, a group of Soviet geologists under the leadership of A. Adamovich and V. Chekhovich conducted a geological survey at a scale of 1:50 000. Chekhovich carried out

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a geological survey on a scale of 1:50 000, the resulting geological map served as a basis for the execution of subsequent studies.

In the years 1963-1965, under the direction of Soviet geologists V. Kenariev and later A. Dioxin, an orientation exploration of the Merceditas, Piloto, Loro, and Yarey refractory chromite deposits was carried out. In 1964 a tachymetric survey of all these deposits was carried out, obtaining a topographic base at a scale of 1:1,000 that allowed the estimation of resources; however, the resources of refractory materials existing in this region of the country were not considered (Pons Herrera, 1999, p. 41).

In the years 1978-1981 in the Merceditas deposit, exploration was carried out by drilling wells from the surface and advancing subway mining workings (adits, galleries, shafts, and vein cutters). The wells were drilled with a 40 X 20 grid, taking into consideration the wells drilled in 1963-1965. The number of measured resources most indicated was 503 800 tons (Ramirez Perez & Pons Herrera, 2018).

The former Empresa Minera Holguín (later Empresa Cromo Moa), began the extraction of these resources in 1981 and between 1992-1995 detailed prospecting and exploration works were carried out to guarantee 200.0 MT of chromite ores in the proven category and 50.0 MT of these ores in the probable category, but refractory ores, present in these deposits, were never considered.

From 1999 to 2000, detailed exploration works were carried out in the southwestern flank of the Merceditas Underground Chrome, which had planned to guarantee 100.0 MT in proven category and 60.0 MT in probable category, which was one of the last works developed before the closing of the mining operations, leaving a large amount of refractory material in the main mines of the Moa-Baracoa region (Merceditas, Amores, Cayo Guam, and Potosi, among others).

The existence of large quantities of refractory materials in this region of the country, with the possibilities of being used by Cuban metallurgical industries (see Figure 1), constitutes the main problem and motivation for the development of this research.

Figure 1. Tailings dams of material with refractory properties, accumulated in areas of old Chromite Mines in the Moa-Baracoa Region.

RESEARCH MATERIALS AND METHODS

The main physical-chemical, mineralogical and thermal characteristics of the refractory chromite production rejects from the Moa-Baracoa region were studied through research projects, taking as case studies the Merceditas, Amores, and Cayo Guam areas.

The chemical and mineralogical analyses were developed through ICP and X-ray diffraction techniques, from the laboratories of the Center for Research and Development of the Nickel Industry (CEDINIQ). Thermal analyses were carried out at the Centro de Investigación para la Industria Minero Metalúrgica (CIPIMM). The granulometric analyses were carried out at the Minerals and Materials Processing Laboratory of the University of Moa.

ANALYSIS AND DISCUSSION OF THE RESULTS

The Mining-Metallurgical Environmental Liabilities generated by the refractory chromite extraction activities in the Moa-Baracoa region, according to their physical-chemical and mineralogical characteristics, can be classified as: “Serpentinite Reject”, which will facilitate the understanding of the results shown below.

The physical characterization of this material, showed as the main results, the predominance of fractions - 4 + 0.35 mm, after the crushing process to which it is subjected to obtain typical granulometric classes of sands and refractory paints for foundry, shown in a summarized way in the following table, the results of the studied zones.

Table 1. Average particle size characteristics of the “Serpentinite rejects” generated by the Refractory Chromite industry in the Moa-Baracoa region.

Tamices (mm)	Merceditas (g)	Amores (g)	Cayo Guam (g)	Promedio (%)	Salida (%)	Retenido (%)	Cernido (%)
- 0,074	120	118	119.6	119.2	3.21	3.21	100
- 0,088 +0,074	136.5	137.8	68.4	114.2	3.072	6,282	96.79
- 0,10 +0,088	31.8	35.6	16.5	27.97	0.752	7,034	93.72
- 0,35 +0,10	368.7	439.8	320	376.2	10.12	17.15	92.97
- 1,98 +0,35	1200	1200	1200	1200	32.27	49.42	82.85
- 4 +1,98	1400	1100	1200	1200	32.27	81.7	50.58
- 6 +4	333.6	369.4	329.8	344.3	9.259	90.95	18.31
+ 6	235.4	435.1	339.1	336.5	9.051	100	9.05
Total (g)	3,826.0	3,736.0	3,593.0	3,718.0	100	-	-

As a result of this study, three fundamental granulometric groups can be distinguished: a fine fraction, smaller than 0.088 mm, which represents 3.072 % by weight and is used as filler for refractory paints; a second intermediate granulometric group, made up of fractions larger than 0.084 mm and smaller than 4 mm, representing 32.27 %, which are used as foundry sand and aggregate for the construction of mortars, and a third group of coarser fractions, larger than 4 mm, representing 9.25 % by weight, which has been used as construction material.

Table 2 shows the average chemical composition, in %, of the Serpentinite rejects studied, characterized by the predominance of SiO_2 and MgO, which indicate the presence of serpentine and olivine minerals in this type of residue.

Table 2. Average chemical composition (%) of the main compounds present in the serpentinite rejection studied.

Sample	NiO	CoO	MnO	Al_2O_3	Cr_2O_3	SiO_2	MgO	Fe^{2+}	Fe^{3+}
Serpentinite rejection	0.574	0.02	1.64	0.86	0.621	29.16	33.201	2.02	3.34

The mineralogical analysis allowed to determine the mineralogical phases present in this environmental liability, where the presence of serpentine and olivine minerals, mainly characteristic of the rocks and minerals of the Moa-Baracoa region, stands out, as shown in Figure 2.

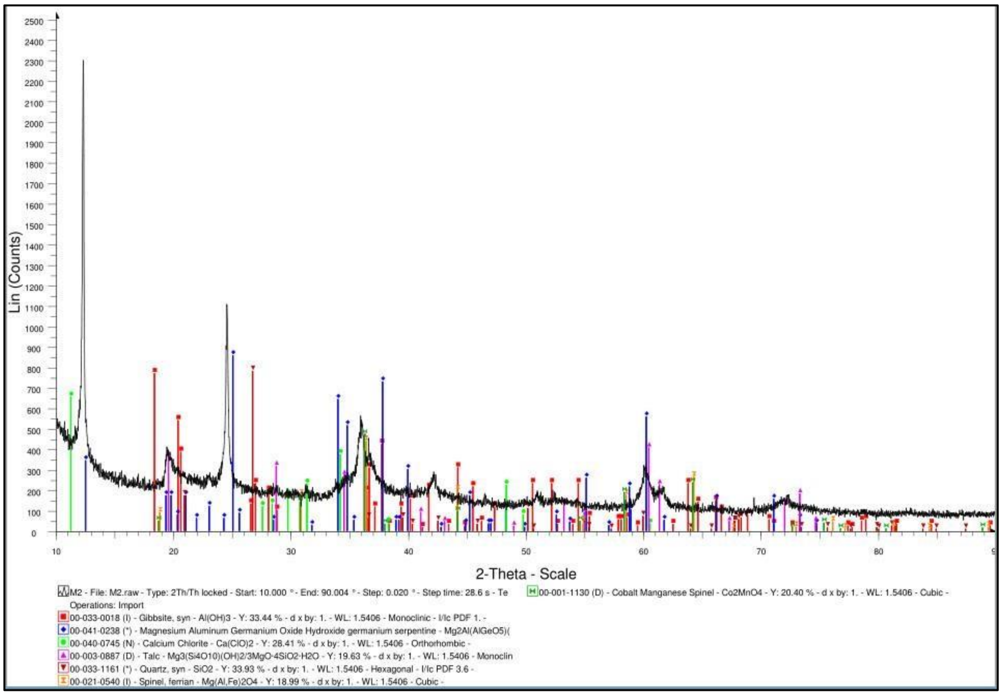

Figure 2. The typical diffractogram of the "Serpentinite rejects" studied.

Table 3 shows the average semi-quantitative mineralogical composition of the "Serpentinite rejects", expressed in percent (%).

Table 3. Semi-quantitative mineralogical composition of the "Serpentinite rejects" from the Moa-Baracoa region.

Mineralogical phases	Chemical formula	Content of mineralogical phases (%)
Olivine (Forsterite)	$MgO.SiO_2$	33.44
Calcium chlorite	$Ca(ClO)_2$	28.41
Talc	$Mg_3(Si_4O_{10})(OH)_2/3MgO \cdot 4SiO_2 \cdot H_2O$	19.63
Quartz	SiO_2	33.93
Iron Spinel	$Mg(Al,Fe)_2O_4$	18.99

Cobalt spinels and Manganese	Co_2MnO_4	20.40

As a result of the mineralogical studies, it was possible to summarize that the main mineralogical phases present in the Serpentinite Rejects, correspond to serpentine minerals with more than 48 %, followed by quartz with 33.93 % and olivine minerals with a content of 33.44 %; iron spinels represent 19 %, while cobalt and manganese spinels constitute 20.4 %.

The thermal behavior of this environmental liability made it possible to determine the decomposition mechanism of this material, as well as the mass losses and the main effects that are verified with the increase in temperature, as shown in Figure 3.

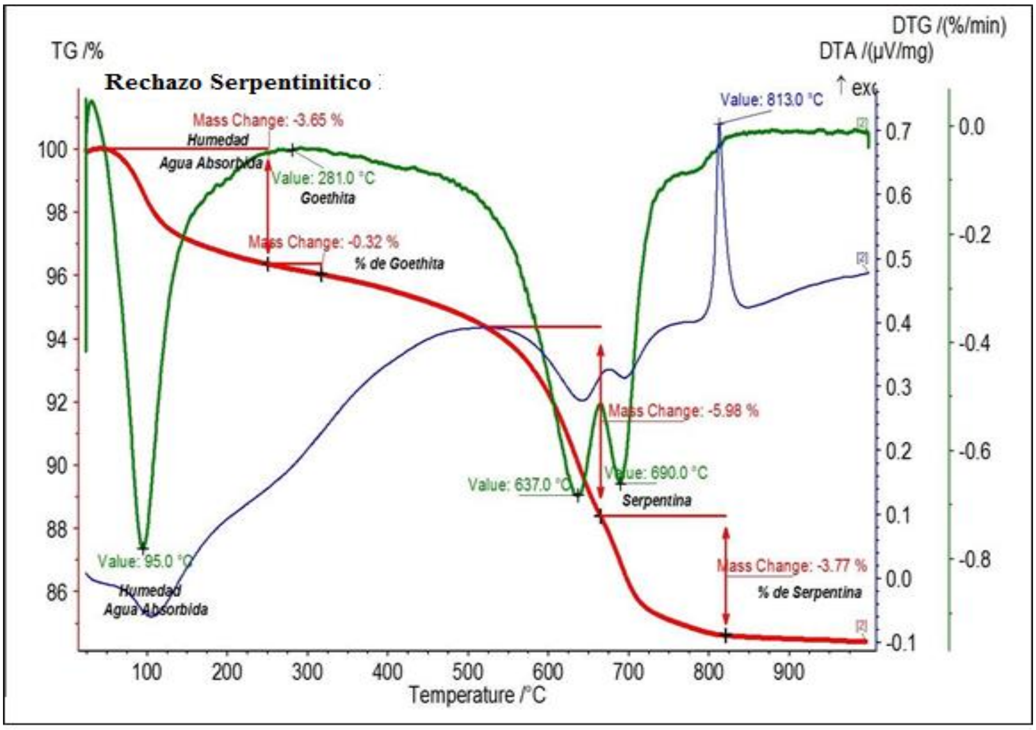

Figure 3. Typical thermogram of the environmental liability "serpentinite rejection" studied.

The mechanism of thermal decomposition of serpentine minerals or rejects from the old refractory chromite production in the Moa-Baracoa region is mainly associated with serpentine and olivine minerals, and the stages of this mechanism are defined as follows:

First stage or step: In the 50 - 240 ºC range, the first endothermic effect occurs, with a mass loss of 3.65 %, which reaches its greatest speed at 95 ºC, the maximum value of the effect, which is associated with the elimination of the hygroscopic water present in this material.

Second stage, which is the most important and longest, it is subdivided into two fundamental stages:

- Firstly, it takes place in the temperature range between 510 ºC - 650 ºC, where an endothermic effect is verified, with a maximum peak at 637 ºC, with a total mass loss equivalent to 5.98 %, all of which is associated with the elimination of the internal or structural water that serpentine minerals have, in this case lizardite; and chrysotile,

- The second step occurs between 650 and 840 ºC, with two important effects, one endothermic with a maximum peak at 690 ºC, and another exothermic with a maximum effect at 813 ºC, which together have a mass loss of 3.77 %, all of which is associated with the beginning and culmination of the recrystallization process of the serpentine and olivine minerals, which represent a total of 75 % within this rejection.

Overall, this second stage is linked to the restructuring or recrystallization of serpentine and olivine minerals, with a total mass loss of 9.65 %, a process very characteristic of the minerals of the Moa-Baracoa region, associated with the olivine present in the parent rocks that make up these deposits, which confirms the results of Pons Herrera et al. (2022); (2018); (2000).

By way of summary, it can be concluded that the “Serpentinite rejects” from the old extraction and processing plants of refractory chromite in the Moa-Baracoa region have a fairly similar physical-chemical and mineralogical composition, which means that the variation in the average content of the components from one deposit to another is quite discrete.

Thermally, the rejects from the Merceditas, Amores and Cayo Guam Zones have a very similar decomposition mechanism, which justifies their use as refractory material in metallurgical companies. This similarity can be appreciated in Figure 4.

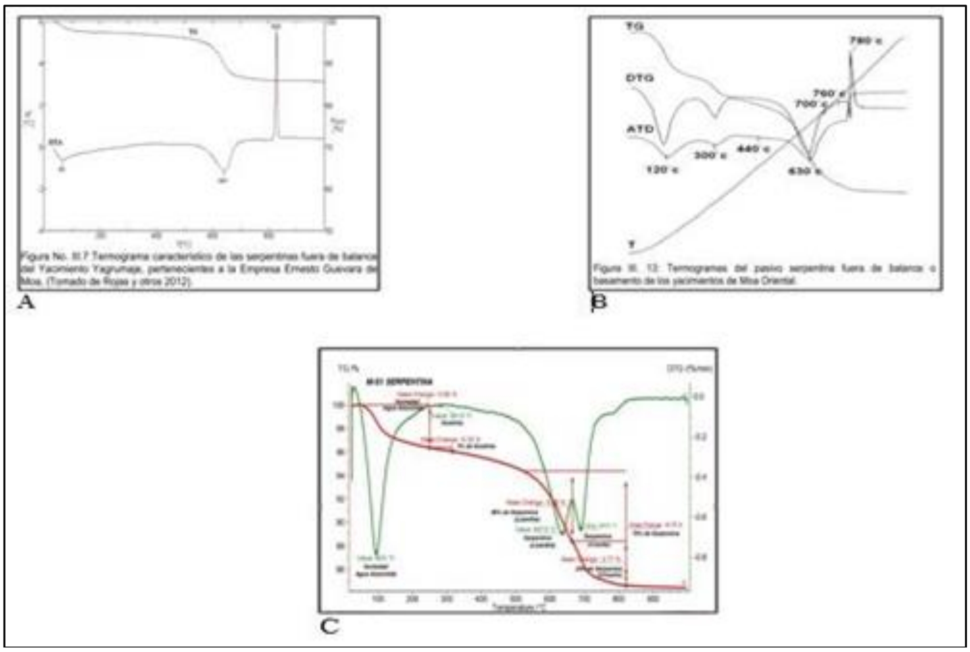

Figure 4. Comparison between thermograms of the “Serpentinite Rejects”.

A-) Merceditas; B-) Amores and C-) Cayo Guam..

CONCLUSIONS

The results of characterization and comparison with other similar PAMMs, allow taking preliminary decisions on the possible use of these, as refractory and construction material, specifically, sands and paints for foundry, mortars, concrete blocks, pavements, railroad ballast, fluxes, etc., after complying with the requirements demanded to these types of products and their certification, by the authorized institutions in Cuba.

The analyzed rejects have a predominance of serpentine and olivine minerals, which have been used as refractory and construction materials in Cuba and the world, which is why their use is recommended in the proposals.

Additionally, these liabilities accumulate in large quantities in abandoned mining areas, affecting the ecosystem of the region; therefore, the results of this research will contribute to decision-making on their future industrial use.

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