MN MINING WASTES AS AN INDUSTRIAL INCOME FOR CONCRETE PRODUCTION: INVENTORY OF WASTE-DUMPS AND RESOURCES ESTIMATION IN THE IBERIAN PYRITE BELT, SW SPAIN

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ABSTRACT

The present work aims to evaluate the possibility of achieving an environmental and economic valorisation of Mn-wastes through their recycling for concrete production. The study area is located in the Spanish sector of the Iberian Pyrite Belt (IPB), where there are numerous abandoned mine-waste dumps, resulted from exploitation of manganese mines. The methodological approach included field surveys for elaborating an inventory and a general map of all the abandoned exploitations, remote sensing methods for identifying old mines and for estimation of affected areas; and laboratory analyses for characterizing the mine wastes regarding evaluation of their potential as filler for concrete production.

The obtained results indicated the existence of 149 mines, representing a total affected area of 235 ha. Among these waste dumps, about eleven of them have more than 10 000 m^3 of Mn-gangue with chemical composition compatible with the normative for concrete production. The recycling of such wastes may accomplish two main purposes: to supply the market with low cost aggregates and, simultaneously, to contribute for the environmental rehabilitation of the affected areas.

Keywords: Manganese gangue, mining waste-dumps, recycling, filler, Iberian Pyrite Belt.

INTRODUCTION

The Iberian Pyrite Belt (IPB), extending from N of Seville – in Spain – to SW of Portugal is one of the largest metallogenic regions in the world. It is known by their giant massive vulcanogenic sulphide ore deposits. Nevertheless, this world-class metallogenic province was also intensively exploited for manganese ores. This historic activity made of Spain the first Mn producer by the end of 19 century (Fig. 1).

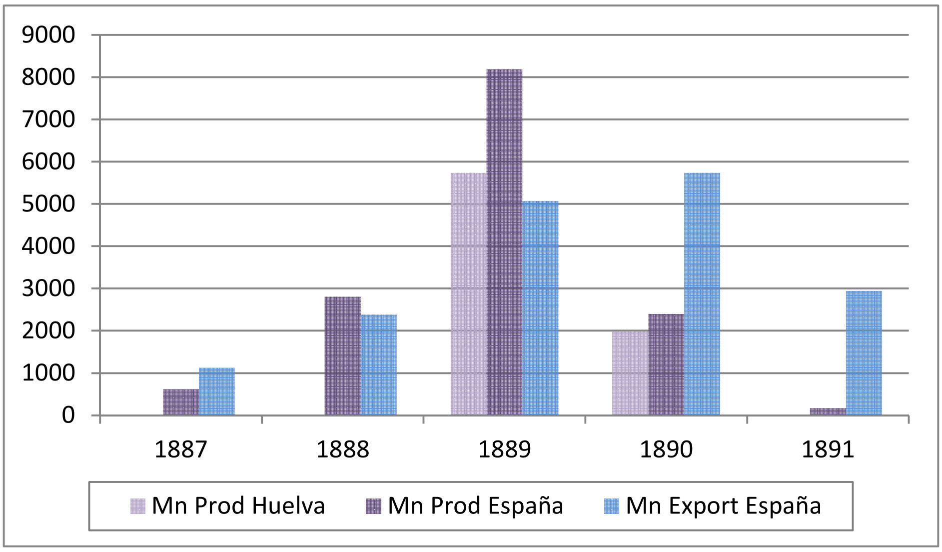

Fig. 1- Production and exportation of Mn ore (ton) in Spain and in the Huelva province during the most productive period (years 1887 – 1891). Data obtained from Estadística Minera de España, 1861-1973 [1].

The Iberian Pyrite Belt, especially the Huelva province, was the most productive manganese region in Spain. In fact, in some years Huelva produced all the Spanish ore. The manganese exploitation lasted until the eighties of the XX century, although suffering the typical cycle patterns as observed for other metals. The most intensive mining works took place until the sixties. In general, higher productions and prices can be assigned to world war and post war periods, until the decline registered from the 70's that led to the closure of mines.

At the present, the world manganese production is focused mainly in China, Australia, Brazil and African countries as stated by the production data in table 1, obtained from USGS: Mineral Commodity Summary (2011).

Table 1 - Mn World production. Data from USGS: Mineral Commodity Summary (2011).

Production (Mt/year) (2011)					
China	Australia	South Africa	Gabon	India	Brazil
2.8	2.4	2.2	1.4	1.1	0.83

In this context, nowadays all the mines in the Iberian Pyrite Belt are abandoned. From this activity resulted the waste dumps that accumulate high amounts of wastes, mainly composed by chert. The mine wastes are relatively inert and, consequently, do not generate the typical contamination problems observed in metallic mining. Nevertheless, the dispersion of wastes throughout the IPB produces scenarios of landscape degradation. Therefore, waste dumps represent an environmental liability, which needs rehabilitation.

On the other hand, the mineralogy and chemistry of such wastes may be indicative of its potential to be used as aggregates for concrete production. Silica is generally the major component of chert gangue, representing more than 80% in accordance with [2]. This siliceous composition associated with low levels of alkalis and aluminium and some proportion of iron and manganese [3] may raise the interest in recycling such wastes.

Concrete is a mixture of water, cement and aggregate, with this last representing between 60-80% in volume. The amount and type of aggregate control the properties of the concrete, namely regarding its cost. Such proportion of aggregates demands for constant supply of raw materials. So, the opportunity of the present work is justified by the following circumstances:

- the existence of numerous abandoned waste dumps needing rehabilitation;

- the inert composition of manganese gangue, which is derived from the lithology and mineralogy of the exploited ore deposits;

- the existence of market demanding for low cost aggregates;

- social and environmental contexts that value the waste recycling;

- economic advantages of extracting materials from the waste chain by incorporating them in industrial processes.

So, the aim of the present study is to evaluate the possibility of achieving an environmental and economic valorisation of Mn-wastes through their recycling for concrete production. Considering the above circumstances, the following specific objectives were defined: i) to identify all the Mn-mines demanding for rehabilitation in the Spanish sector of the IPB; ii) to accomplish an inventory form in order to systemize the most relevant information about each mine, including geographic, geological, mining and geotechnical data; iii) to elaborate a global map with location of all the mines; iv) to determine the areas affected by mining activities and occupied by waste dumps; v) to estimate waste volumes available for recycling; vi) to evaluate the potential of the wastes as filler for concrete production.

Study area

The study area is located in the Iberian Pyrite Belt, specifically in the Huelva Province (Fig. 2). Although known by the massive sulfide ore deposits within the Volcano-Sedimentary Complex (e.g., [4, 5]), the geology of the IPB also favoured the occurrence of stratabound Mn-ore deposits.

Fig. 2 – Location of study area in the central sector of Iberian Pyrite Belt, SW Spain.

There are siliceous slates grading to jasper at the top of the stratigraphic sequence [6]. Mn deposits occur in the oxidation zones over carbonates and silicates, such as rhodochrosite ($MnCO_3$) or rhodonite ($Mn_2(SiO_3)_2$) lenses in jasper. Also, pyrolosite (MnO_2), psilomelane (MnO_2 H_2O), and “wad” appear at the top of the sequence as secondary ore minerals. More detailed information about the geology of Mn-oxide deposits can be found in [7] and [8].

Manganese exploitation was both by underground and open-cut mining methods. The majority of exploitations were of small size, with the highest mining interest focused on oxides in chert [2]. Ambitious and irrational mining contributed to high volume waste dumps very rich in silica, since the siliceous ores were often neglected.

Methods

The methodology included bibliographic and field surveys as well as sampling procedures and laboratory work for physical-chemical and mineralogical characterization. The following steps were considered:

i) Review of the existent geological, mining, mapping and photogeological data;

ii) Elaboration of review maps based on the previous step;

iii) Field work, including:

a. location and delimitation of mining areas,
b. characterization, classification and mapping of mining structures,
c. obtaining aerial photographs (photographic fly),
d. sampling at the waste dumps.

iv) Integration of field data in a global map;

v) Record of data in an inventory file;

vi) Estimation of the Mn-gange that may be available as resource in the major waste-dumps;

vii) Laboratory work, comprising:

a. Preparation of samples for chemical and mineralogical analyses, including homogenization, granulometric classification and milling (until fraction <75µm),
b. mineralogical analysis by X-ray diffraction (XRD),
c. chemical analysis for SiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, and MgO, performed by X-ray fluorescence (XRF),
d. morphological and elemental characterization by scanning electron microscopy (SEM),

viii) Laboratory assays, involving petrographic description of the samples and chemical and mechanical tests, such as alkali-silica reactivity and resistance to fragmentation.

Results and discussion

Inventory of mines and mapping

The present work allowed to inventory 149 Mn-mines in the Huelva province, which were located in an interactive global map (Fig. 3) built over a digital terrain model. Each point gives information about the respective mine, including its code and name.

The distribution of Mn-abandoned mines indicates very accurately the Vulcano sedimentary Complex outcrops within the Iberian Pyrite Belt. The mine dispersion shapes the structures, which describe the large anticlinal and synclinal systems, namely the ones of Puebla de Guzmán, Valverde, and Riotinto.

To describe each mine an inventory file was produced, which compiles different type of information, namely: name and code, location, UTM coordinates, municipality and administrative situation, number of topographic map (in the respective file from Instituto Cartográfico Andaluz; Spain). In addition, there are data about the mining exploitation (open cut or underground), geologic context, and the presence of waste dumps and other remnant structures. Moreover, each file provides the total affected area and the volume of wastes. The file also comprises a map of the mining area, with delimitation of waste-dumps and other affected areas.

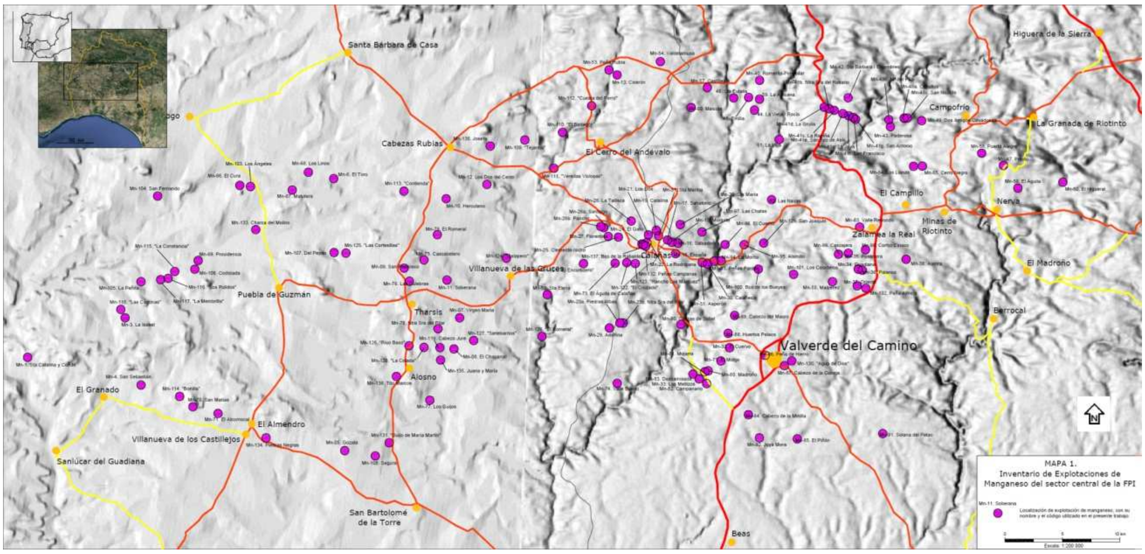

Fig. 3 – Global map with the distribution of Mn-mines in the Huelva province. The map is available at scale 1:25 000. UTM coordinates -30-S.

Estimation of affected areas and volume of resources

A total area of about 235 ha was calculated as being directly affected by the Mn-mining activity, which represents 0.023% of the Huelva province surface area. At each site, the affected area is variable, but most of the mines are of small size. In 96% of them there are less than 4 ha of affected land. A total volume of 1 200 000 m^3 of Mn-wastes was obtained.

For the ten major mines, table 2 provides an estimation of the area specifically affected by the presence of waste dumps. Each mine is identified by name and code. The volume of wastes accumulated in each one is also presented.

Table 2 – Surface areas affected by waste-dumps and volume of wastes.

Code	Name	Area of waste dumps (m^2)	Volume of wastes (m^3)
Mn-001	Santa Catalina and Conde	10 500	45 000
Mn-003	La Isabel	10 500	37 000
Mn-006	El Toro	8600	25 000
Mn-026a	Santiago	5000	17 500
Mn-026b	Pancho	3700	11 000
Mn-027	Florentina o Sierpe	10 400	60 000
Mn-032	Preciosa o El Cuervo	5900	41 000
Mn-036	Palanco	8000	28 000
Mn-041a	La Joya (Soloviejo)	55 400	830 000
Mn-047	Pepito	500	1500

Chemical composition of the Mn-wastes

Table 3 presents the chemical composition of the filler obtained with samples from three selected waste dumps (Mn-001 - Santa Catalina; Mn-026a - Santiago; and Mn-041a - La Joya –Soloviejo). In the three cases, silica is the major component (> 38%). The alkaline elements occur in small proportions (< 9%) and all the samples have some content in iron (4-6%) and manganese (3-18%).

Table 3 – Chemical composition (major components) of the Mn- filler obtained by XRF.

	Oxides (wt%)						
Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	K_2O	CaO	MgO
Mn-001	74,9	7,98	6,31	4,44	1,16	0,83	0,46
Mn-026a	38,1	8,74	3,47	18	1,58	8,89	3,07
Mn-041a	68,4	15,3	3,77	3,05	3,24	0,82	1,02

The global chemical composition is compatible with the indications established by technical normative, such as the EHE-08 [9], for production of structural concrete and the PG-3 [10], for bituminous concretes. Therefore, the obtained results show the potential of these Mn-wastes to be used as aggregates in concrete production.

In fact, stress-strain tests performed with concrete doped with Mn-wastes as filler [2] already indicated good performance regarding resistance to compression.

Conclusion

The present study presents an inventory of Mn-mines in the Iberian Pyrite Belt, as well as an evaluation of the remnant mine wastes as potential resources for concrete production. The following conclusions were achieved:

- There are 149 abandoned Mn-mines, which were located in a global map.
- More than 235 ha of surface area are affected by Mn mining activity.
- Mn-wastes represent a total volume of 1 200 000 m^3.
- The Mn-wastes have chemical and physical properties compatible with their recycle as filler for structural and bituminous concretes.
- Preliminary laboratory results suggest the fitness of Mn-gangue to replace raw aggregates as filler. Nevertheless, further work must be developed in order to accurately characterize all the Mn-wastes in the IPB and to evaluate the effect of Mn-filler in the chemical and mechanical properties of the new mixtures.

REFERENCES

[1] Estadística Minera de España del año 1896. (1897) Ministerio de Fomento. Dirección General de Agricultura, Industria y Comercio. Junta Facultativa de Minería. Madrid. 148 pp. [Consulta: 15 septiembre 2013]. Available in: http://www.igme.es/internet/estminera/informes/1896.pdf.

[2] Salguero, F.; Grande, J. A.; Valente, T.; Garrido, R.; de la Torre, M., Fortes, J.C.; Sánchez, A. Manganese gangue materials from waste-dumps in the Iberian Pyrite Belt – Applications as filler for concrete production. Construction & Building Materials, 54, pp. 363-368, 2014.

[3] Leistel, J.M., Marcoux, E., Deschamps, Y. Chert in the Iberian Pyrite Belt. Mineralium Deposita 33, pp 59-81, 1998.

[4] Sáez R., Almodóvar G.R., Pascual E. Geological constraints on massive sulphide genesis in the Iberian Pyrite Belt. Ore Geol Rev,11, pp. 429–51, 1996.

[5] Sáez R., Pascual E., Toscano M., Almodóvar G.R. The Iberian type of volcanosedimentary massive sulphide deposits. Miner Deposita, 34, pp. 549–70, 1999.

[6] Moreno, C., González, F. Estratigrafía de la Zona Sudportuguesa. In: VERA J.A. (ed pral) Geología de España. Madrid. Sociedad Geológica de España; Instituto Geológico y Minero de España. Capítulo 2.7.3., pp. 201-20, 2004..

[7] Pinedo and Vara J. Piritas de Huelva. Su Historia, Minería y Aprovechamiento. Summa, Madrid, 1963.

[8] Tornos F. Environment of formation and styles of volcanogenic massive sulfides. The Iberian Pyrite Belt. Ore Geol Rev., 26, pp. 259–307, 2006

[9] EHE-08 (2008). Instrucción de hormigón estructural EHE-08. Ministerio de Fomento Madrid. [Consulta 6 noviembre 2013]. Available in: http://www.fomento.es/MFOM/LANG_CASTELLANO/ORGANOS_COLEGIADOS/CPH/instrucciones/EHE_es/

[10] Comité Técnico AEN/CTN 83 Hormigón. UNE-EN 12390-3:2009/AC 2011. Testing hardened concrete. Part 3: Compressive strength of test specimens. AENOR, 2011.