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PRELIMINARY STUDIES ON THE UTILIZATION OF SILICOMANGANESE SLURRY

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Abstract: *Silico-manganese sludges are a waste resulting from the ferroalloy industry, more precisely from the manufacture of silico-manganese. From a technological point of view, they come from the sludge resulting from the filtration of furnace gases. From a chemical point of view, they are made up of a large number of combinations of manganese and silicon. The manganese content varies widely between 5-35% MnO. Due to the fact as there are limitations for the manganese content in waters and soils, the presence of these sludge deposits constitutes a permanent risk of environmental contamination. In addition to the definitive closure (greening) of the deposit, there is also the possibility of valorizing this waste. The present paper presents the preliminary research carried out to identify a sustainable technology for the recovery of useful elements from the sludge.*
Key words: *environmental contamination, manganese, manganese recovery, silico-manganese, sludge, slurry*

1. Introduction

The metallurgical industry is facing major problems that are not strictly related to a crisis of raw materials and energy resources but to the stringent requirements for environmental protection. The development of the metallurgical industry is conditioned by solving the major problems arising from the industry-environment relationship, being strictly directed at the control of pollution and the protection of natural and energetic resources. The small and pulverulent waste, mainly from the steel industry but also from the mining and energy industry, due to the high content of iron, manganese, carbon and various oxides (elements useful in the production process of cast iron or steel) should be called by-products and be considered components of natural capital because they can be exploited in the steel industry.

The ecological concept applied to the steel industry involves the development of closed-loop production technological flows in which no waste should be disposed of, all by-products should be continuously reused and no waste should be discharged into the environment. In specialized literature, this system is called "waste free steel industry". Finding efficient solutions from an economic and ecological point of view for technological flows in the steel industry is currently a major concern. Adequate management in terms of waste management and recovery, completely eliminating storage will lead to the protection of natural resources and the recovery of those consumed, thus reducing costs and the impact of disposed waste on the environment. [1].

The concern for compliance with the legislative requirements regarding environmental protection and the need to harmonize the processes of economic progress, with the rational management of material and energy resources, must lead to the valorization of waste through technologies that offer both from an economic and ecological point of view, the optimal solution.

It is necessary to promote technologies that ensure: rigorous waste management, controlled storage of all categories of waste, reduction at the source of the quantity and harmfulness of the produced waste, the most advanced recycling of the resulting waste by re-introducing it in various stages of the technological flow, thus ensuring the protection of natural resources of raw materials and increasing the degree of use of waste by transforming it into raw materials for other industries.

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The continued depletion of mineral resources, rising energy costs and strictly environmental regulations have resulted in increased efforts to recover metals.

2. Silicomanganese production

S.C. FERAL S.R.L. operates in the field of Ferrous Metallurgical Industry producing ferroalloys. The company is located in the industrial area of the city of Tulcea Western Platform, Taberei street no. 2.

The objective produces raw non-ferrous metals from ores, through metallurgical processes, through the FERO I and FERO II processing sections with an average annual production capacity of approx. 240,000 tons of alloys, 2400 tons of powder/slag briquettes [2].

This industry produces and markets: ferroalloys (silicomanganese, ferromanganese), powders and slags low in manganese oxide. About 99% of the unit's production is destined for export. The main uses of the developed ferroalloys are in the metallurgical industry to obtain steels, using them as a deoxidizer and/or alloying material [1]. The basic raw material is: manganese ore, concentrated manganese ore, coke, quartzite, limestone, manganese slag.

The slag dump and silicomanganese dust dump represent a fixed anthropomorphic source, with periodic emissions of pollutants in the form of particles whose frequency and intensity depends on meteorological conditions. Factors favoring pollutant migration to receptors are strong winds and precipitation. On the dust dump belonging to S.C. Feral S.R.L., nothing has been stored since 2012 and contains approximately 830,000 tons of silicon manganese dust [3].

Silicomanganese (SiMn) is an alloy composed primarily of silicon (Si), manganese (Mn), and iron (Fe). It is produced by smelting in a submerged electric arc furnace and is used extensively in the steel industry due to its beneficial properties. Here are the key details about silicomanganese:

Composition:

- Silicon (Si): Typically, between 10-30%
- Manganese (Mn): Usually, around 60-70%
- Iron (Fe): The remainder, with trace amounts of other elements such as carbon, sulfur, and phosphorus.

Production Process: The primary raw materials for producing silicomanganese are manganese ore, silica (quartz), and coke. These materials are smelted in a submerged electric arc furnace, where high temperatures facilitate the reduction of manganese and silicon from their oxides. [4] The molten alloy is then refined to achieve the desired chemical composition and is typically cast into ingots or other forms for further processing. Uses in the Steel Industry:

- Deoxidizer: Silicomanganese is used to remove oxygen from molten steel, preventing the formation of undesirable oxides.
- Alloying Element: It adds manganese and silicon to steel, improving its strength, hardness, and resistance to wear and corrosion.
- Desulfurizer: Manganese helps to remove sulfur from steel, improving its overall quality.

Benefits:

- Improved Mechanical Properties: Enhances tensile strength, ductility, and toughness.

In the present work, the preliminary tests will be presented for the identification of a technology for the valorization of silicomanganese dust resulting from the purification of gaseous effluents stored in the silicomanganese dust dump [5].

Analyzing the existing market for manganese products, it was found that in the last year the price of its ores has decreased significantly. In this context, the material in the warehouse can no longer be used as such, not even after a simple classification. If before it was possible to exploit products with a content of more than 22% manganese, at the present time the price offered for such material is below 30 USD/t (transported to the port), with no purchase interest. Reasonable purchase prices are offered for products with over 42% manganese and in rare cases over 37% manganese.

3. Establishing the characteristics of the initial material

In order to determine the characteristics of the material stored in the silicomanganese dust dump, 7 samples were taken from its entire surface (Fig. 1). The samples were processed in the chemistry laboratory of the University of Petroșani by X-ray fluorescence spectrometry (XRF) using a Rigaku Supermini 200 spectrograph.

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Fig. 1. Sample for analysis

After the chemical analysis, the following chemical compositions of these samples resulted (Table 1):

Table 1. Results of the chemical analysis of the initial samples

Component	**MU**	**Sample**						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Mn	%	19.461	18.610	15.388	20.005	2.8240	13.652	18.527
SiO_2	%	20.777	24.962	29.175	18.682	76.239	28.703	50.481
$Al2O_3$	%	0.3990	0.5570	1.3380	0.7420	0.4750	1.6050	0.8870
S	%	1.1060	0.7930	0.4520	0.6240	0.8950	0.8340	0.7040
P	%	0.0260	0.0430	0.0340	0.0230	0.0470	0.0320	0.0320
Fe	%	2.3310	2.6210	3.6460	2.0670	3.9630	5.3080	3.2460

From the presented results, it is concluded that the tested material is very inhomogeneous both in terms of manganese content and the ratio between the contents of different chemical elements.

Next, an average sample of samples 1, 2, 3, 4, and 7 was made and also sample 7 was retained for further granulometric tests.

4. Preliminary manganese recovery tests

4.1 Densimetric separation tests

Densimetric separation is a process used to separate solid materials of different densities. This process uses a fluid (usually air or water) to separate materials based on their density. Dense materials will sink, while less dense materials will float. The densimetric tests were performed with bromoform, which is a liquid with a density of 2.89 g/cm^3 [6].

The results obtained after the densimetric separation in bromoform are presented in Table 2:

Table 2. Results of densimetric separation in bromoform

Parameter	**MU**	**Heavy Fraction**	**Light Fraction**	**Original**
		Share [%]		
		17.73	82,27	100,00
Mn	%	25.43	14,08	18,47
SiO_2	%	13.31	50,08	36,26
Al_2O_3	%	0.68	2,35	1,72
S	%	0.44	0,61	0,54
P	%	0.05	0,05	0,05
Fe	%	3.28	4,70	4,17
Extraction of Mn	%	24.41		

From the obtained results, it can be observed that the material is relatively homogeneous, so that by densimetric separation, a concentrate with an acceptable manganese content does not result. Also, metal extraction has very little value.

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4.2 Granulometric separation tests

Size separation is a technique used to separate solid particles based on their size. This is essential in many industries, including mining and materials processing, to obtain products of uniform size or to remove impurities. [7]

Particle size separation is based on the use of sieves, filters, or other equipment to sort particles according to their size. Larger particles are retained by the sieve, while smaller particles pass through them [4].

To carry out the test, a quantity of 400 g of material from sample 7 was weighed, which was separated into 4 granulometric classes (-75 microns, +75 microns, +1mm, +3.15mm).

After the granulometric separation, the following results were obtained (Table 3):

Table 3. Results of particle size separation

Parameter	**MU**	**Granulometric class**			
		Share			
		- 0.075 mm	0.075 - 1 mm	1 - 3.15 mm	+ 3.15 mm
		6.61	24.80	27.72	40.87
MnO	%	24.98	24.05	23.96	23.63
SiO_2	%	49.36	50.22	50.73	50.65
Fe_2O_3	%	4.09	4.09	4.06	4.13
CaO	%	2.95	2.94	2.97	2.95
K_2O	%	1.57	1.59	1.58	1.58

From the obtained results it is very clear that there are no notable differences in the manganese contents of different granulometric classes.

4.3 Magnetic separation tests

Magnetic separation is a separation technique used to separate magnetic from non-magnetic materials. It is a common process in industry for mineral separation, metal recycling and waste processing. This method is based on the differences in the magnetic susceptibility of different materials [4].

Magnetic separation uses magnetic forces to attract ferromagnetic materials (such as iron, nickel, and cobalt) or paramagnetic materials into a magnetic field. Diamagnetic and non-magnetic materials are not affected by the magnetic field and remain separated.

Magnetic Separation Methods:

- Wet Magnetic Separation: Materials are mixed with water to form a slurry, which is passed through a magnetic separator.

- Dry Magnetic Separation: Materials are passed directly through a magnetic separator without being mixed with water.

Depending on the strength of the magnetic field, the magnetic separation can be:

- High Intensity Separation: Use of high intensity magnetic separators to separate materials with low magnetic susceptibility. It is used for the separation of paramagnetic minerals and for the cleaning of non-metallic minerals [6].

- Low Intensity Separation: Low intensity magnetic separators are used to separate strongly magnetic materials. Equipment: Permanent magnetic separators, electromagnets [6].

The preliminary magnetic separation tests were performed in a weak magnetic field (classic permanent ferrite magnet) for all 4 particle size fractions shown in table 3. The results obtained from these tests are shown in Tables 4, 5, 6 and 7:

Table 4. Results of magnetic separation in magnetic field for particle size fraction – 0.075 mm.

Parameter	**MU**	**Magnetic fraction**	**Non-magnetic fraction**	**Original**
Extraction	%	46.24	53.76	100.00
MnO	%	27.11	23.25	24.98
SiO_2	%	46.11	51.53	49.36
Fe_2O_3	%	4.14	4.08	4.09
CaO	%	2.92	2.98	2.95
K_2O	%	1.58	1.58	1.57
Mn extraction	%	50.17		
Mn extraction relative to total sample	%	3.32		

Table 5. Results of magnetic separation in magnetic field for particle size fraction 0,075 – 1 mm.

Parameter	MU	Magnetic fraction	Non-magnetic fraction	Original
Extraction	%	21.20	78.80	100.00
MnO	%	27.11	23.25	24.05
SiO_2	%	46.11	51.53	50.22
Fe_2O_3	%	4.14	4.08	4.09
CaO	%	2.92	2.98	2.94
K_2O	%	1.58	1.58	1.59
Mn extraction	%	23.90		
Mn extraction relative to total sample	%	5.93		

Table 6. Results of magnetic separation in magnetic field for particle size fraction 1 – 3,15 mm.

Parameter	MU	Magnetic fraction	Non-magnetic fraction	Original
Extraction	%	23.08	76.92	100.00
MnO	%	27.11	23.25	23.96
SiO_2	%	46.11	51.53	50.73
Fe_2O_3	%	4.14	4.08	4.06
CaO	%	2.92	2.98	2.97
K_2O	%	1.58	1.58	1.58
Mn extraction	%	26.11		
Mn extraction relative to total sample	%	7.24		

Table 7. Results of magnetic separation in magnetic field for particle size fraction + 3,15 mm.

Parameter	MU	Magnetic fraction	Non-magnetic fraction	Original
Extraction	%	13.04	86.96	100.00
MnO	%	27.11	23.25	23.63
SiO_2	%	46.11	51.53	50.65
Fe_2O_3	%	4.14	4.08	4.13
CaO	%	2.92	2.98	2.95
K_2O	%	1.58	1.58	1.58
Mn extraction	%	14.96		
Mn extraction relative to total sample	%	6.11		

From all these tests it is found that both the extraction in the metal and the concentration of manganese in the concentrates have low values.

5. Hydrometallurgical processing tests

Within this experimental cycle, only one sulfuric acid leaching test was performed.

For this purpose, a quantity of approximately 10 grams of material was taken and placed in an acidic solution of sulfuric acid 1:2. The reaction proceeded energetically, with strong release of heat [8]. After the reaction stopped, the acid solution was separated by filtration from the unreacted fraction. Dissolved metals were separated by selective precipitation. The pH of the solution was adjusted using 40% KOH to 3.2-3.4 to obtain iron precipitation. After filtering the iron, the pH of the solution was adjusted to a value between 5 and 5.5 for aluminum precipitation. After filtering the aluminum, the pH of the solution was adjusted to 8-9 to obtain the precipitation of manganese. The results obtained from these tests are presented in Table 8:

From the results of the preliminary leaching test, a high purity manganese concentrate and a residue very poor in manganese, consisting of a mixture of quartz and coke powder were obtained. In conclusion, the only method by which silico-manganese sludge can be exploited is the hydrometallurgical one, provided that high-purity, high-value products are obtained [9].

Table 8. Results of manganese separation by sulfuric acid leaching.

Component	Manganese concentrate	Final residue
MnO	99.878	1.067
SiO_2	0.018	94.648
Fe_2O_3	0.087	0.875
CaO	0.007	0.775
K_2O	0.011	1.555

6. Conclusions

The material in the dumps is inhomogeneous in terms of granulation, being made up of brown-colored manganese powders, gray-colored quartz powders, brown-colored spherical silico-manganese pellets, pieces of slag and other foreign bodies (waste of construction materials).

Following the physical and chemical analyses, manganese concentrations of approximately 18% were obtained, a value that corresponds to that indicated in the test reports provided by the beneficiary.

By simple granulometric classification, significant increases in the manganese content are not obtained, except to the extent that part of the foreign bodies and larger slag grains are removed.

Separation tests indicated that manganese can be concentrated by granulometric and magnetic classification methods in a weak magnetic field up to a concentration of 24 - 27% Mn, which is absolutely unsatisfactory.

Through hydrometallurgical processes, a high-purity manganese concentrate can be separated, from which economically valuable products can be obtained, such as manganese dioxide, manganese sulfate or the manganese salt of diethyldiaminetetraacetic acid with applications in agriculture.

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