



INTEGRATED APPROACHES FOR MANGANESE RECOVERY FROM SILICO-MANGANESE SLUDGE

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Abstract: This paper analyses the possibilities for the valorisation of silico-manganese sludge generated during ferroalloy production, with the aim of recovering manganese and reducing environmental impact. The study focuses on the comparative evaluation of physical and hydrometallurgical methods and the identification of an integrated process scheme.

The investigated material was characterised by physicochemical and mineralogical analyses (XRF, XRD, SEM), revealing a heterogeneous system with a variable manganese content (3.6-20.5%) and a predominantly siliceous matrix. Physical separation methods (size classification, density separation, and magnetic separation) were investigated, together with hydrometallurgical processes based on acid leaching and selective precipitation. The results show that physical methods lead to limited manganese enrichment, with low recovery rates (20-25%), due to its distribution throughout the material and its association with difficult-to-separate phases. In contrast, hydrometallurgical processes enable efficient manganese recovery, achieving yields of up to 95-96% and high-purity products (approximately 99% MnO equivalent).

The results demonstrate that integrated treatment schemes combining physical pretreatment and hydrometallurgical recovery provide the most effective route for manganese recovery from silico-manganese sludge. This approach supports the valorisation of industrial waste as a secondary resource within circular economy and sustainable resource-use strategies.

Keywords: silico-manganese sludge; manganese recovery; hydrometallurgical processing; acid leaching; selective precipitation; circular economy

1. Introduction

Metallurgical waste materials have attracted increasing attention in recent years due to their environmental impact and their potential as secondary resources. The growing demand for critical raw materials and the need to reduce industrial waste storage have intensified interest in the recovery of valuable elements from metallurgical residues within circular economy strategies [1, 2, 3].

Silico-manganese sludges generated during ferroalloy production represent a category of industrial residues containing potentially recoverable manganese fractions. These materials are characterised by a heterogeneous structure and by the association of manganese-bearing phases with a predominantly siliceous matrix, which complicates conventional recovery processes [4, 5, 6]. In addition, long-term storage of these residues may contribute to environmental degradation and to the loss of potentially valuable secondary resources.

In Romania, significant quantities of silico-manganese sludge are still stored in historical industrial deposits formed during former metallurgical activities. One representative example is located in the Tulcea area, where fine-grained manganese-bearing residues remain deposited in spoil heaps associated with past ferroallurgical operations.

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Several studies have investigated the recovery of manganese from similar materials using both physical separation techniques and hydrometallurgical processes [7, 8, 9, 10, 11, 12, 13, 14]. Physical methods such as particle size classification, density separation and magnetic separation are attractive because of their relatively simple operation and lower processing costs. However, in the case of silico-manganese sludges, their efficiency remains limited due to the fine particle size of the material and the close association between manganese-bearing phases and siliceous compounds [8, 9, 10].

Under these conditions, hydrometallurgical treatment becomes a more suitable option for manganese recovery from this type of material. Previous studies have shown that acid leaching combined with redox conditioning and selective precipitation can ensure efficient manganese recovery from secondary resources [11, 12, 13, 14].

However, relatively few studies comparatively evaluate both physical and hydrometallurgical approaches within a single integrated recovery scheme for silico-manganese sludges originating from historical industrial deposits. In particular, the relationship between the limited efficiency of physical pre-treatment methods and the superior performance of hydrometallurgical recovery stages remains insufficiently discussed for this category of secondary resources. Therefore, the present study aims not only to evaluate manganese recovery efficiency, but also to highlight the role of integrated treatment flowsheets within circular economy strategies focused on metallurgical waste valorisation.

The present study comparatively evaluates the performance of physical and hydrometallurgical methods applied to silico-manganese sludges originating from historical deposits and proposes an integrated approach for manganese recovery and sludge valorisation.

2. Characterisation of the material

The material investigated consists of silico-manganese sludges originating from the production of manganese-based ferroalloys and stored in industrial spoil heaps. These materials are generally present as fine particles with a heterogeneous structure, influenced by variations in industrial processing conditions and long-term storage.

The physicochemical characterisation of the material was performed using XRF, XRD and SEM analyses in order to determine the chemical composition, identify the mineral phases and examine the morphology of the investigated samples.

The chemical analyses showed that the investigated material contains manganese mainly in oxide forms, together with high amounts of silicon dioxide and smaller quantities of iron and aluminium oxides. Similar characteristics have been reported for silico-manganese sludges and slags in previous studies, where the predominance of siliceous phases and the variability of manganese content were associated with differences in industrial processing conditions and storage history [5, 6, 15].

The analysed samples exhibited noticeable variations in chemical composition, confirming the heterogeneous nature of the deposit. Some areas were richer in manganese, while others contained predominantly siliceous material. The indicative values of the main chemical compounds identified by XRF analysis are presented in Table 1.

Table 1. Range of variation and average values of the main chemical components

Component	Range (%)	Average (%)
Mn	3.64 – 20.47	15.50
SiO ₂	18.88 – 83.54	35.57
Al ₂ O ₃	0.39 – 1.77	0.86
Fe	2.06 – 6.04	3.31
S	0.42 – 1.17	0.77
P	0.023 – 0.051	0.034

The mineralogical investigations also highlighted the presence of manganese oxide and silico-oxide phases closely associated with the siliceous matrix. This type of association makes the physical release and concentration of manganese more difficult during conventional separation processes.

Particle size analysis showed that the material is composed mainly of fine and medium fractions, without major differences in manganese content between the analysed size classes. These observations suggest that manganese is dispersed throughout the material rather than concentrated in a particular fraction.

Overall, the investigated silico-manganese sludges can be considered complex heterogeneous materials, characterised by the uneven distribution of manganese-bearing phases within a predominantly siliceous matrix. Under these conditions, physical separation methods alone are not sufficient to achieve efficient manganese recovery.

3. Limitations of physical separation methods

Physical separation methods are frequently used in the recovery of waste materials due to their technological simplicity and low costs. In the case of silico-manganese sludges, these methods have been investigated to assess the possibility of concentrating manganese through particle size classification, density separation and magnetic separation. Experimental physical separation tests were carried out on the investigated sludge in order to evaluate the possibility of manganese concentration through conventional physical methods.

The results obtained show that the distribution of manganese according to particle size is relatively uniform, with no concentration in a distinct particle size fraction. Similar results have also been reported in the literature for fine manganese-bearing residues, where the authors highlight that the association of manganese with the siliceous matrix limits the efficiency of particle size classification and conventional physical separations [8, 9, 10]. Although the fine fractions have a slightly higher manganese content, the differences observed are moderate and do not allow for the production of a significant concentrate through simple particle size classification alone.

The experimental investigations carried out on the analysed sludge confirmed that manganese remains distributed throughout both the fine and coarse fractions, without the formation of a clearly enriched particle size class. This behaviour limited the efficiency of the physical concentration stages applied in this study.

3.1 Density separation

Densimetric separation leads to a partial enrichment of manganese in the heavy fraction, where the manganese content increases significantly compared to the initial material. However, this fraction accounts for approximately 17-18% of the total mass, and the manganese recovery rate remains limited, standing at approximately 24%.

The obtained results showed that only partial concentration of manganese could be achieved through densimetric separation, as a significant fraction of manganese remained associated with the lighter siliceous material. Consequently, the overall efficiency of the process remained relatively low.

The investigated material showed a strong association between manganese-bearing phases and the siliceous fraction, which limited the transfer of manganese into the heavy product during separation.

3.2 Magnetic separation

In the case of magnetic separation, the results indicate a modest increase in the manganese content of the magnetic fraction, due to the presence of weakly paramagnetic manganese-bearing phases or those associated with iron compounds.

The experimental observations suggest that the weak magnetic response of the investigated material is related both to the mineralogical composition of the sludge and to the fine particle size of the analysed fractions. Similar behaviour has also been reported in the literature for fine manganese-bearing materials, where the efficiency of magnetic separation depends strongly on particle size, mineralogical composition and the association of manganese with siliceous phases [9, 10].

Even under favourable conditions, manganese recovery remains limited, with higher values being obtained mainly in the very fine fractions. Under the investigated conditions, manganese recovery remained around 10%, confirming the limited efficiency of magnetic separation for this type of material.

Overall, the limited efficiency of physical methods is determined by the mineralogical characteristics of the material, in particular the association of manganese with the siliceous matrix and its distribution across the entire particle size spectrum. These factors lead to low enrichment and low recovery rates, confirming that physical methods cannot, on their own, ensure the efficient utilisation of silico-manganese sludges.

4. The hydrometallurgical approach to manganese recovery

The limitations observed for physical separation methods indicate the need for processes capable of mobilising manganese from the material structure. In this context, hydrometallurgical treatment represents a suitable approach based on the selective dissolution of manganese-bearing phases followed by impurity separation.

Hydrometallurgical experiments were carried out on the investigated silico-manganese sludge in order to evaluate manganese dissolution efficiency and impurity separation behaviour under controlled process conditions. The hydrometallurgical processes applied to silico-manganese sludges are based mainly on acid leaching using mineral acids such as sulphuric acid or hydrochloric acid.

The recovery efficiency of the hydrometallurgical process depends on several operating parameters, including acid concentration, temperature, leaching time and solid-to-liquid ratio. Higher acid concentrations and elevated temperatures usually favour the transfer of manganese into solution, especially in the case of manganese-bearing phases dispersed within the siliceous matrix. At the same time, the use of excessively severe leaching conditions may lead to increased reagent consumption and to the co-dissolution of impurities such as iron and aluminium.

Previous hydrometallurgical studies have shown that acid leaching is effective for transferring manganese from solid residues into solution and represents one of the most widely used methods for the recovery of manganese-bearing secondary materials [11, 12, 13, 14]. In the case of materials with a predominantly siliceous matrix, single-stage leaching is often insufficient because part of the manganese remains associated with poorly soluble phases.

4.1 Two-stage acid leaching

In the present study, an integrated hydrometallurgical approach was applied in order to improve manganese recovery while maintaining acceptable process selectivity. The adopted process was based on two-stage acid leaching followed by redox conditioning and selective precipitation stages.

During the first leaching stage, readily accessible manganese fractions are dissolved from the sludge matrix, while the second stage contributes to the mobilisation of manganese remaining in the solid residue after the initial treatment. This approach allows an increase in overall manganese recovery without excessively intensifying the operating conditions.

The applied experimental scheme was evaluated on the investigated silico-manganese sludge in order to assess manganese recovery efficiency and impurity separation behaviour. The obtained results confirmed that the successive application of the two leaching stages improved manganese dissolution compared with single-stage treatment approaches.

The general flow diagram of the integrated hydrometallurgical process used for manganese recovery from silico-manganese sludges is presented in Figure 1.

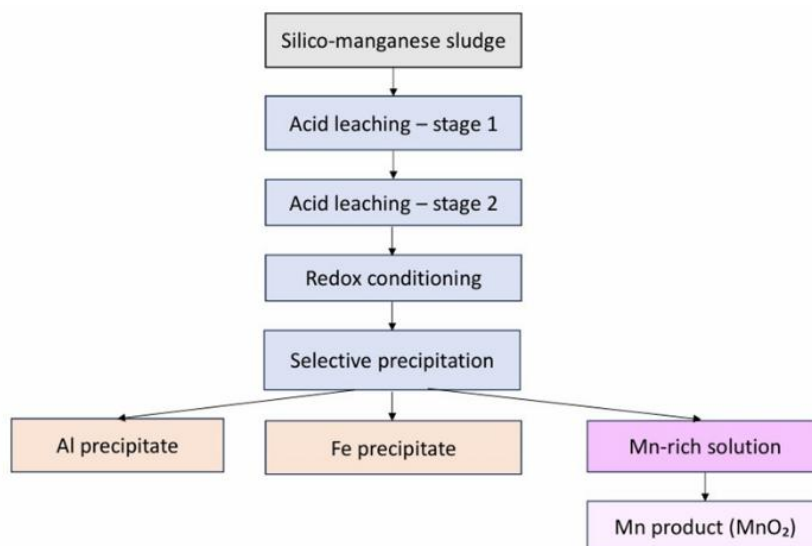


Fig. 1. Simplified flowsheet of the integrated hydrometallurgical process for manganese recovery from silico-manganese sludge

The flowsheet presented in Figure 1 illustrates the successive stages of manganese recovery applied in this study, beginning with two-stage acid leaching and followed by redox conditioning and selective precipitation. The proposed scheme was designed to improve manganese dissolution efficiency while limiting the transfer of impurities into the final product. At the same time, the successive treatment stages allow the progressive separation of iron- and aluminium-containing species prior to the final manganese recovery step.

4.2 Redox conditioning and selective precipitation

The diagram presented in Figure 1 summarises the principal stages of the integrated process applied for manganese recovery and for the gradual removal of metallic impurities.

In the applied process, the redox conditioning stage contributed to improving impurity separation and maintaining manganese in solution prior to the final recovery stage. By adjusting the redox conditions and pH, iron- and aluminium-containing species could be progressively separated, while manganese remained predominantly in solution until the final precipitation step [13, 14].

The experimental results showed that the proposed treatment scheme allows efficient manganese recovery, with recovery yields of approximately 95-96%. At the same time, the final manganese-rich product exhibited a high purity of approximately 99% MnO equivalent, making it suitable for potential value-added applications. The product composition was expressed as MnO equivalent according to XRF analytical convention, although the applied oxidation and precipitation conditions may favour the formation of higher manganese oxide phases, including MnO₂-type compounds.

The experimental results confirmed that the successive application of leaching, redox conditioning and selective precipitation stages improved both manganese recovery and product purity compared with physical separation methods alone.

The good performance of the hydrometallurgical process is mainly related to its ability to dissolve manganese-bearing phases that cannot be efficiently separated by physical methods. Compared with physical separation techniques, the applied process allows the recovery of a significantly larger fraction of manganese and leads to the formation of a high-purity manganese-rich product.

The application of integrated recovery schemes of this type may also contribute to reducing the quantities of sludges stored in historical industrial deposits and to limiting their associated environmental impact. In addition, the recovery of manganese from secondary materials is consistent with current efforts aimed at reducing the consumption of primary raw materials and improving resource utilisation efficiency [1, 2, 3, 16].

From this perspective, the proposed approach supports the valorisation of industrial waste materials and can be associated with current circular economy strategies in the mining and metallurgical sectors.

Overall, the obtained results indicate that hydrometallurgy represents the most effective approach for the recovery of silico-manganese sludges. The integration of leaching and selective separation stages allows the development of technologically viable recovery schemes adapted to this type of material. The comparative performance of the investigated recovery methods is summarised in Table 2.

Table 2. Comparative performance of physical and hydrometallurgical methods for manganese recovery

Process	Mn recovery (%)	Remarks
Density separation	~24	Limited enrichment
Magnetic separation	~10	Highly dependent on particle size
Integrated hydrometallurgy	~95–96	High purity (~99% MnO equivalent)

The comparative analysis presented in Table 2 clearly highlights the superior performance of the integrated hydrometallurgical route compared with conventional physical separation methods. While physical processes may contribute to preliminary enrichment and volume reduction, they are not sufficient to ensure efficient manganese recovery due to the complex mineralogical structure of the sludges. Consequently, the integration of physical pretreatment with hydrometallurgical recovery stages represents a more suitable technological solution for the valorisation of these secondary resources.

The differences between the efficiency of physical methods and that of the integrated hydrometallurgical process are shown comparatively in Figure 2.

Although the obtained results highlight the high efficiency of the hydrometallurgical process, industrial-scale implementation still requires further evaluation of reagent consumption, operating costs and the management of resulting waste streams. In addition, the compositional variability of the sludge may influence process performance and may require adjustment of operating conditions according to the characteristics of the treated material. These aspects represent important directions for future investigations.

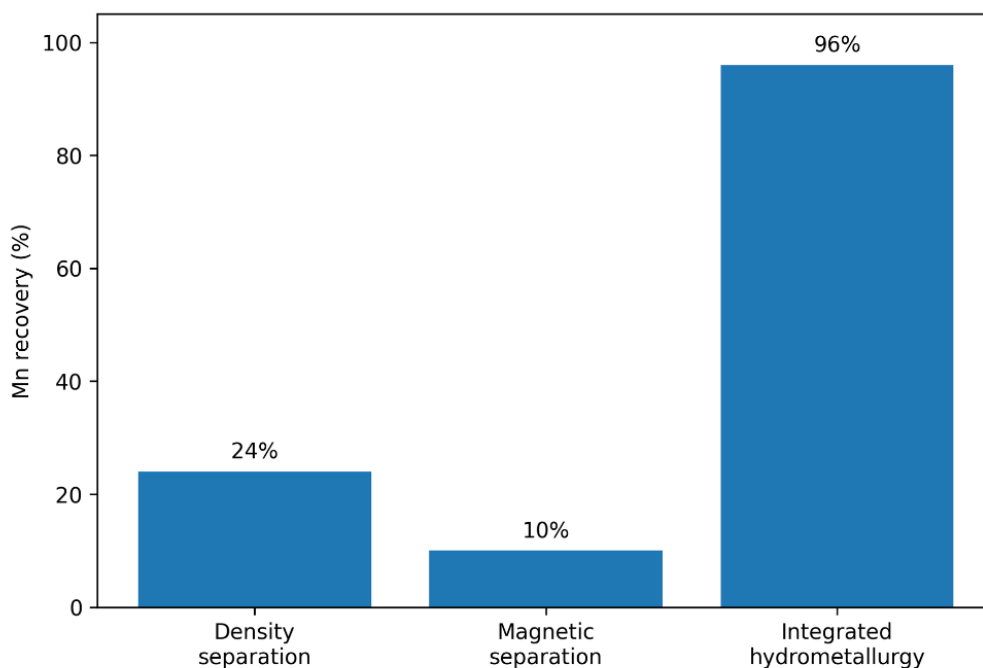


Fig. 2. Comparative manganese recovery obtained by physical and hydrometallurgical methods applied to silico-manganese sludge

5. Conclusions and future directions

The obtained results highlight the complex nature of silico-manganese sludges and confirm the difficulties associated with recovering manganese using only conventional physical separation methods. The investigated material showed a relatively uniform distribution of manganese throughout the particle size fractions, together with a strong association between manganese-bearing phases and the predominantly siliceous matrix. Under these conditions, physical separation methods such as density or magnetic separation led only to moderate enrichment and relatively low recovery rates.

The applied hydrometallurgical approach proved significantly more effective for the recovery of manganese from this type of material. The combination of two-stage acid leaching, redox conditioning and selective precipitation allowed the progressive dissolution of manganese-containing phases and the controlled removal of impurities from solution. As a result, high manganese recovery yields of approximately 95-96% were achieved, together with the production of a high-purity manganese-rich product expressed as approximately 99% MnO equivalent according to XRF analysis.

The study also highlights the potential of silico-manganese sludges as secondary raw materials that may be reused instead of being stored for long periods in industrial deposits. The recovery and valorisation of these materials may contribute both to reducing environmental impact and to improving the utilisation of manganese-containing industrial residues within current circular economy strategies.

At the same time, the obtained results indicate that integrated treatment schemes combining physical pretreatment and hydrometallurgical recovery represent a more suitable approach for this category of waste materials than the application of physical methods alone.

The proposed integrated flowsheet highlights the complementary role of physical pre-treatment and hydrometallurgical recovery stages. While physical methods contribute mainly to preliminary enrichment and volume reduction, hydrometallurgical treatment ensures the effective dissolution, selective separation and high recovery of manganese. From this perspective, the obtained results demonstrate the technological potential of integrated recovery schemes for the future industrial valorisation of silico-manganese sludge deposits.

Future research should focus on the optimisation of operating parameters, particularly reagent consumption, process selectivity and the control of impurity separation stages. Additional studies regarding process scalability, economic feasibility and industrial implementation are necessary for the practical application of this type of recovery process. Nevertheless, the obtained results confirm that silico-manganese sludges may represent valuable secondary manganese resources within future circular economy and sustainable metallurgy frameworks.

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