

Hydrometallurgical recovery of high-purity manganese-rich products from silicomanganese production sludge

Mariana I. Dumitrache ¹, Maria Lazăr ², Camelia Traistă ³

¹ University of Petrosani, Doctoral School, Department of Mines, Oil and Gas, 332111, Petrosani, Romania

^{2,3} University of Petrosani, Faculty of Mine, Department of Environmental Engineering and Geology, 332111, Petrosani, Romania

Corresponding author: mariana.ionela.dumitrache@gmail.com, MarianaDumitrache@upet.ro (Mariana I. Dumitrache)

Abstract: Historical silicomanganese sludge deposits represent a potential secondary source of manganese, although its recovery is complicated by the heterogeneous chemical and mineralogical characteristics of the material. This study investigated the chemical, mineralogical and particle size characteristics of silicomanganese sludge and comparatively evaluated physical and hydrometallurgical approaches for manganese recovery. Thirty-five samples collected from the investigated deposit were characterised, and a representative composite sample was used for particle size classification, magnetic separation, density separation and hydrometallurgical experiments. Manganese was distributed throughout the entire particle size range, with limited enrichment in the finer fractions. Magnetic and density separation provided only partial pre-concentration, with overall manganese recoveries of approximately 27.4% and 24.4%, respectively. Hydrometallurgical treatment was investigated using HCl-water and aqua regia-water leaching systems, followed by sequential alkaline precipitation with KOH. Fe- and Al-bearing species were removed at controlled pH before recovery of the manganese-rich precipitate at pH 9–10. Under the most favourable conditions, the recovered products contained approximately 99–100% MnO equivalent, as determined by XRF, while the principal residual impurities were generally below 0.1%. Both leaching systems produced highly purified manganese-rich products, while the HCl-water route achieved comparable results without the use of aqua regia. The results demonstrate that physical separation provides only limited manganese pre-concentration, whereas acid leaching followed by selective purification and precipitation represents a promising route for the recovery of high-purity manganese-rich products from historical silicomanganese sludge.

Keywords: silicomanganese sludge, manganese recovery, hydrometallurgical processing, leaching, mineral characterization

1. Introduction

Silicomanganese is an important ferroalloy used in steel production as both a deoxidising agent and an alloying element (Olsen et al., 2007). Its production generates dust and sludge collected by gas-cleaning systems, whose composition and properties depend on the raw materials and furnace operating conditions (Gasik, 2013; Kero et al., 2019). The resulting variability directly affects the behaviour of these residues during separation and recovery processes and therefore influences the selection of an appropriate recovery route.

1.1. Overview of the silicomanganese production process

Silicomanganese is produced in submerged arc electric furnaces through the carbothermic reduction of manganese and silicon oxides derived from manganese ores and silica-bearing raw materials. The furnace charge typically consists of manganese ore, quartz or other silica sources, carbonaceous reducing agents such as coke or coal, and fluxes, which together provide the conditions required for the reduction reactions and alloy formation (Olsen and Tangstad, 2004; Olsen et al., 2007).

The smelting process is carried out at temperatures of approximately 1500–1700 °C, where manganese and silicon oxides are reduced to form the silicomanganese alloy, while the gangue components and fluxes combine to produce slag (Olsen and Tangstad, 2004; Gasik, 2013). During the process, fine particulate matter is generated and transported by the process gases to the gas treatment system, where it is collected as dust or sludge, depending on the gas cleaning technology employed (Kero et al., 2019).

The amount and composition of the collected material depend on the characteristics of the raw materials, furnace operating conditions, and gas-cleaning technology. For example, Wallin et al. (2021) reported an industrial SiMn sludge generated by wet scrubbing of furnace off-gas containing 37.61 wt.% MnO and 32.26 wt.% SiO₂, together with smaller amounts of C, K₂O, Al₂O₃, MgO, and Fe₂O₃. Such compositions indicate that SiMn dusts and sludges may retain substantial manganese values and can therefore be considered potential secondary resources for manganese recovery.

1.2. Mechanisms of silicomanganese slurry formation

The formation of silicomanganese sludge results from physical and chemical processes occurring during smelting, gas transport, and gas cleaning. Element distribution between the alloy, slag, and dust phases is governed by furnace conditions and by the thermochemical behaviour of the elements present in the raw materials. In a pilot-scale study conducted in a 440 kVA submerged arc furnace, Ma et al. (2018) investigated the distribution of 51 elements between the alloy, slag, and dust phases, demonstrating the strong influence of element volatility and furnace conditions on their partitioning.

Two main mechanisms contribute to the formation of the particulate material. Volatile elements and compounds may enter the gas phase at high furnace temperatures and subsequently condense as the process gas cools. Ma et al. (2018) showed that volatile elements such as K, Na, Rb, and Cs preferentially report to the dust phase through vaporisation and subsequent condensation or oxidation. In parallel, mechanical entrainment transports fine particles originating from the raw materials and process products into the furnace off-gas. Manganese furnace dust has consequently been described as a combination of volatile species and mechanically entrained fine particles collected from the furnace off-gas during manganese alloy production (Shen et al., 2005; Kero et al., 2019).

The combined action of volatilisation, condensation, and mechanical entrainment produces a heterogeneous particulate material whose composition and mineralogy reflect both the thermochemical behaviour of the elements during smelting and the physical transport of fine particles. This heterogeneity contributes to the variable characteristics of the collected dust and sludge and influences their subsequent processing behaviour.

1.3. Composition and characteristics of silicomanganese sludge

Silicomanganese sludge and furnace dusts exhibit considerable compositional variability depending on the raw materials, furnace operating conditions, and gas-cleaning system. Ordiales et al. (2016) reported manganese contents of approximately 20–40 wt.% in ultrafine oxidized dust generated during ferromanganese and silicomanganese production. Similarly, Shen et al. (2005) reported an average Mn content of 33.4 wt.% in dried manganese furnace dust, together with approximately 20 wt.% carbon and 1.29 wt.% Zn. These results illustrate the substantial compositional variability of Mn-bearing residues and their potential as secondary manganese resources.

The recovery behaviour of these materials also depends on the mineralogical forms in which manganese occurs. Shen et al. (2005) identified Mn-bearing phases including manganosite (MnO), hausmannite (Mn₃O₄), and rhodochrosite (MnCO₃), whereas investigations of SiMn submerged arc furnace dust have identified braunite and jacobsonite together with silicate phases such as quartz and diopside (Nkosi et al., 2011). The occurrence of manganese in chemically and mineralogically different phases can influence its response to physical separation and subsequent hydrometallurgical treatment.

Consequently, chemical composition, mineralogical characteristics, and particle-size distribution should be established before selecting a recovery route. Such characterisation provides the basis for assessing the applicability of physical separation methods and for selecting appropriate conditions for the subsequent recovery of manganese-bearing compounds.

1.4. Recovery and valorisation approaches for silicomanganese sludge

Recovery strategies for manganese-bearing dusts and sludges include internal recycling through agglomeration and furnace reintroduction, thermal treatment, physical separation, and hydrometallurgical processing. The applicability of these routes depends strongly on the composition and mineralogy of the residue, particularly the occurrence of Mn-bearing phases, residual carbon, silicates, and volatile elements such as Zn (Shen et al., 2005; Zhang and Cheng, 2007). Hydrometallurgical routes are of particular interest because they enable manganese dissolution, solution purification, and subsequent recovery as higher-value manganese compounds, including manganese dioxide (Zhang and Cheng, 2007; Önal et al., 2021).

Internal recycling after agglomeration represents a direct route for the valorisation of manganese-bearing furnace dusts. Briquetting, pelletisation, or sintering facilitates the reintroduction of fine material into the furnace while reducing particle entrainment during handling and smelting. However, the recirculation of volatile elements, particularly Zn, can restrict repeated recycling and requires appropriate control of the recycled material (Shen et al., 2005; Shen et al., 2007). More recently, Xu et al. (2025) investigated the carbothermic reduction of carbon-containing silicomanganese dust briquettes and reported a reaction fraction of approximately 90% at a C/O molar ratio of 1.2, showing the potential of controlled agglomeration and reduction for recycling SiMn dust.

Hydrometallurgical processing provides an alternative route for recovering manganese through acid leaching, followed by solution purification and conversion into higher-value manganese compounds. For pelletised SiMn submerged arc furnace dust, Nkosi et al. (2011) reported Mn extraction of up to approximately 49% by atmospheric leaching with dilute H_2SO_4 . Higher dissolution efficiencies have been obtained for related Mn-bearing residues under reductive conditions. Ghafarizadeh et al. (2011), for example, achieved complete Mn leaching from ferromanganese electric-arc-furnace dust using 2 mol/L H_2SO_4 and 0.31 mol/L oxalic acid at 70 °C for 90 min and a liquid-to-solid ratio of 30:1. These results demonstrate the strong dependence of Mn dissolution on the characteristics of the feed material and the selected leaching conditions.

Beyond dissolution, hydrometallurgical flowsheets can include purification of the pregnant leach solution and subsequent recovery of manganese as higher-value products. Önal et al. (2021) demonstrated the production of electrolytic manganese dioxide (EMD) from manganese-bearing furnace fines through a process involving leaching, solution purification, and electrolysis. This route is particularly relevant because it demonstrates that Mn-bearing metallurgical residues can be processed beyond simple metal extraction to obtain manganese dioxide as a defined final product.

Physical separation can also be considered as a pre-concentration step before hydrometallurgical treatment, although its effectiveness depends strongly on the mineralogical associations and liberation characteristics of the material. Kim et al. (2011) investigated mechanical separation of waste silicomanganese slag and showed that physical processing can concentrate Mn-bearing fractions, whereas studies on SiMn furnace dust have demonstrated that manganese may occur in several mineral phases closely associated with silicate and Fe-bearing components (Nkosi et al., 2011). These findings suggest that physical pre-concentration may reduce the amount of material subjected to subsequent leaching when sufficient mineral liberation is achieved, but its applicability to heterogeneous silicomanganese sludge must be evaluated for the specific residue considered.

Valorisation of silicomanganese residues can also reduce the amount of Mn-bearing material requiring long-term disposal and decrease the demand for primary manganese resources. European Best Available Techniques reference documents encourage the recovery and recycling of secondary materials from ferroalloy production when technically and economically feasible (European Commission, 2017). In this context, recovery strategies that combine effective manganese extraction with the management of residual solid fractions are relevant to both resource recovery and waste reduction.

1.5. Novelty and objective of the study

Preliminary investigations on the recovery of manganese from the same type of historical silicomanganese sludge were reported by Dumitrache et al. (2024). That study evaluated particle-size classification, density separation and low-intensity magnetic separation and included a single

hydrometallurgical test based on H_2SO_4 leaching followed by selective precipitation. The physical separation methods provided only limited manganese enrichment, whereas the hydrometallurgical treatment demonstrated the potential for obtaining a highly purified manganese-rich product. The recovered concentrate was reported by XRF as 99.878 wt.% MnO equivalent, with only minor amounts of associated elements.

The present study extends this previous work through a broader sampling and characterisation programme and, particularly, through the investigation of two distinct hydrometallurgical routes based on HCl and aqua regia. Thirty-five samples collected from the historical deposit were used to assess compositional variability, and a representative composite sample was subsequently subjected to detailed chemical and mineralogical characterisation, particle-size classification, magnetic separation and density separation. The HCl and aqua regia leaching systems were investigated separately under different reagent proportions and temperature conditions, followed by selective precipitation and chemical characterisation of the recovered manganese-rich products by XRF.

The objective of the study was to determine how the physicochemical and mineralogical characteristics of the sludge influence its response to physical separation and hydrometallurgical treatment and to compare the two leaching routes in terms of process conditions, impurity removal and the chemical composition and purity of the recovered manganese-rich products. The novelty of the work lies in evaluating HCl- and aqua-regia-based routes on the same representative historical residue through the complete experimental sequence from feed characterisation and leaching to selective precipitation and chemical characterisation of the recovered manganese-rich products. This approach enables comparison of the two routes on the basis of the composition and chemical purity of the recovered products, rather than considering the leaching stage alone.

2. Materials and methods

2.1. Materials

Sampling of the historical silicomanganese sludge deposit was designed to account for the spatial and stratigraphic heterogeneity of the deposited material. The deposit was divided into seven sampling sectors covering the investigated area, and a total of 35 primary samples were collected from locations distributed among these sectors. The sampling campaign was organised by sectors rather than according to a regular fixed-dimension grid; therefore, uniform sampling-grid dimensions are not applicable.

Sampling was carried out by local excavation. Depending on the accessibility and local conditions at each sampling location, material was collected from depths of approximately 30-60 cm. Where necessary, a small excavator was used to expose the subsurface material, followed by manual collection. Sampling locations were selected to include the visually distinguishable layers encountered within each sector and to account for variations in colour, texture and degree of compaction.

The primary samples were individually packaged, labelled according to their sampling sector and location, and transported to the laboratory. Samples originating from the same sector were subsequently combined to obtain seven sector-specific composite samples. The preparation of these samples and of the representative overall composite sample is described in Section 2.2.1.

The initial characterisation of the historical deposit was based on the 35 individual samples. Their chemical composition and particle size distribution were determined to assess the variability of the material across the investigated area. Based on this initial characterisation, a representative overall composite sample was prepared for the subsequent detailed physicochemical and mineralogical analyses, physical separation tests, and hydrometallurgical experiments. The use of the same composite sample throughout the recovery tests allowed the different treatment methods to be compared using the same feed material.

A representative photograph of the overall composite silicomanganese sludge sample used for the subsequent physicochemical characterisation and recovery experiments is presented in Fig. 1. The material consists predominantly of fine, dark-coloured agglomerates with occasional coarse siliceous fragments, illustrating the physical appearance of the composite sample prior to preparation and analysis.



Fig. 1. Representative overall composite silicomanganese sludge sample used for physicochemical characterisation and recovery experiments

2.2. Methods

2.2.1. Preparation of the composite sample

The primary samples collected within each of the seven sampling sectors were combined to obtain seven sector-specific composite samples. Prior to further preparation, the samples were dried at 105 °C to constant mass and subsequently thoroughly homogenised.

Each sector-specific composite sample was reduced by successive manual quartering. After each division, two diagonally opposite quarters were retained and recombined, and the procedure was repeated as required. Further sample reduction was performed using a riffle splitter to obtain a representative subsample from each sector.

The seven sector-specific subsamples were subsequently combined and thoroughly homogenised to obtain the representative overall composite sample. This composite sample was used for the subsequent physicochemical characterisation, physical separation tests and hydrometallurgical experiments. Specific subsamples were prepared from this material according to the requirements of each analytical or experimental procedure.

2.2.2. Chemical analysis by X-ray fluorescence (XRF)

The chemical composition of the 35 individual samples, the representative composite sample, and the fractions obtained during particle size classification and separation experiments was determined by wavelength-dispersive X-ray fluorescence (WDXRF) using a Rigaku Supermini 200 spectrometer equipped with a rhodium (Rh) X-ray tube and wavelength-dispersive analysing crystals for the determination of major and minor elements.

Instrument calibration was performed using certified reference materials with matrices comparable to those of the analysed samples. Matrix corrections were applied using the Fundamental Parameters (FP) method.

The samples were analysed as pressed powder pellets, without prior fusion, in order to avoid possible volatilisation losses and to preserve the original chemical composition of the investigated material.

2.2.3. Mineralogical analysis by X-ray diffraction (XRD)

The mineralogical characterisation of the composite sample was performed by powder X-ray diffraction (XRD). Prior to analysis, the sample was ground to a particle size below 63 µm to ensure adequate sample homogeneity and high-quality diffraction patterns.

The analyses were performed using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in Bragg-Brentano geometry, over a 2θ range of $5\text{--}80^\circ$, with a step size of 0.02° . The acquisition parameters were selected to provide an adequate signal-to-noise ratio and reliable identification of the crystalline phases.

Phase identification was carried out by comparison of the experimental diffraction patterns with the PDF-4 (Powder Diffraction File) database. Semi-quantitative phase evaluation was based on the relative intensities of the characteristic diffraction peaks.

The XRD analysis enabled the identification of the principal manganese-bearing and silicate phases present in the sludge. The mineralogical information obtained was subsequently used to interpret the behaviour of the material during the physical separation and hydrometallurgical recovery experiments.

2.2.4. Particle size analysis

An initial particle size analysis was performed on the 35 individual samples to characterise the granulometric variability of the material across the historical deposit. Based on the variability identified during the initial characterisation of these samples, as discussed in Section 3.3, a representative overall composite sample was used for the subsequent physicochemical characterisation and technological investigations. The particle size distribution of the composite sample was determined using the same sieving procedure to establish the granulometric characteristics of the material used in the subsequent experiments.

Prior to sieving, the samples were dried at 105°C to constant mass. Particle size analysis was performed by dry sieving using a standard series of sieves mounted on a mechanical sieve shaker. The sieve series comprised mesh sizes of 10 mm, 6.3 mm, 3.15 mm, 2.5 mm, 1.25 mm and 0.5 mm, selected to characterise the particle size distribution of the material over the range relevant to the subsequent technological investigations. Particles smaller than 0.5 mm were collected in the receiving pan.

After sieving, the material retained in each particle size class was weighed, and its mass was expressed as a percentage of the total sample mass.

The particle size fractions obtained from the representative composite sample were subsequently analysed by X-ray fluorescence (XRF) to determine the distribution of manganese and the other major chemical constituents as a function of particle size.

2.2.5. Magnetic separation tests

Magnetic separation tests were performed at laboratory scale on the representative overall composite sample to evaluate the potential for pre-concentrating manganese-bearing phases based on differences in magnetic susceptibility between the components of the silicomanganese sludge.

Prior to magnetic separation, the composite sample was dried at 105°C to constant mass and separated by dry mechanical sieving into four particle-size classes: $<0.075 \text{ mm}$, $0.075\text{--}1 \text{ mm}$, $1\text{--}3.15 \text{ mm}$ and $>3.15 \text{ mm}$. The particle-size classes were prepared using the same dry sieving procedure described in Section 2.2.4, with the sieve series adapted to obtain the four size intervals required for the magnetic separation tests.

Each particle-size class was subjected separately to dry magnetic separation using a permanent ferrite magnet generating a low-intensity magnetic field of approximately 0.2 T. The same separation procedure was applied to all four particle-size classes.

For each particle-size class, the magnetic and non-magnetic fractions were collected separately and weighed to determine their mass proportions. Both fractions were subsequently analysed by X-ray fluorescence (XRF) to determine their chemical composition and to evaluate the distribution and recovery of manganese during magnetic separation.

The results were used to assess the influence of particle size on magnetic separation and the potential of low-intensity magnetic separation as a preliminary pre-concentration step for the investigated silicomanganese sludge.

2.2.6. Densimetric separation tests

Density separation tests were carried out on the representative overall composite sample to evaluate the possibility of pre-concentrating manganese-bearing phases based on differences in density between the individual components of the silicomanganese sludge.

The separation was performed using bromoform (CHBr_3) as the heavy liquid, with a density of approximately 2.89 g/cm^3 . A known mass of the dried composite sample was placed in a separation vessel and immersed in the heavy liquid. The suspension was gently agitated and allowed to settle until separation of the particles was achieved.

The process produced two fractions. Particles with a density greater than that of bromoform formed the heavy fraction (sink), whereas particles with a lower density constituted the light fraction (float).

The two fractions were collected separately, thoroughly washed to remove residual bromoform, dried to constant mass and weighed. Their chemical compositions were subsequently determined by X-ray fluorescence (XRF), and manganese distribution and recovery were calculated from the corresponding mass and chemical composition data.

All procedures involving bromoform were carried out in a fume hood in accordance with laboratory health and safety requirements because of the toxicity and volatility of the reagent.

2.2.7. Acid leaching tests

Concentrated hydrochloric acid (37 wt.% HCl) and nitric acid (65 wt.% HNO_3) were used for the preparation of the leaching solutions. Aqua regia was freshly prepared by mixing concentrated HCl and HNO_3 in a 3:1 volumetric ratio. Distilled water was used for the preparation of the HCl-water and aqua regia-water mixtures.

For each leaching experiment, 10 g of the prepared material was contacted with 100 mL of leaching solution, corresponding to a solid-to-liquid ratio of 1:10 (g/mL), or a pulp density of 100 g/L. The experiments were carried out for 120 min under continuous magnetic stirring at 400 rpm.

For the HCl series, concentrated hydrochloric acid (37 wt.% HCl) was mixed with distilled water in different volumetric proportions while maintaining a constant total solution volume of 100 mL. HCl proportions ranging from 25 to 100 vol.% were investigated. The same HCl-water compositions were tested at $25 \pm 2^\circ\text{C}$ and $80 \pm 2^\circ\text{C}$, while the other experimental conditions were kept constant.

A second series of experiments was performed using aqua regia diluted with distilled water in different volumetric proportions, while maintaining the same total solution volume of 100 mL. The proportion of aqua regia ranged from 10 to 100 vol.%. In this experimental series, the reagent proportion and operating temperature varied simultaneously. Therefore, the results were interpreted under the combined experimental conditions, without attributing the observed differences independently to either reagent proportion or temperature.

At the end of each leaching experiment, the solid-liquid suspension was filtered. The solid residue was washed with distilled water, dried to constant mass and weighed. The resulting leach solution was retained for the subsequent selective precipitation procedure described in Section 2.2.8.

Dissolved Mn in the leach solution was not quantified directly by solution-phase analysis. Accordingly, the hydrometallurgical results reported in this study are based on the XRF chemical characterisation of the manganese-rich solid recovered after the subsequent selective precipitation procedure, rather than on a direct determination of Mn concentration in the pregnant leach solution.

The leaching experiments were conducted as individual tests for each experimental condition and were not independently replicated; therefore, experimental standard deviations are not reported. The relatively large number of experimental conditions was intended to establish the overall trends of the investigated systems rather than to provide a statistical assessment of individual conditions.

The experimental results were subsequently used to evaluate the influence of reagent concentration, operating temperature, and leaching-medium composition on the characteristics of the recovered manganese-rich products. The effects of these parameters are discussed in detail in Section 3.7.

2.2.8. Selective precipitation

The leach solutions obtained after HCl and aqua regia treatment were subjected to successive selective precipitation using 40 wt.% KOH solution. The pH was gradually increased under continuous stirring to separate the dissolved metal species according to their different precipitation behaviour.

Iron was first precipitated by adjusting the solution to pH 3.2-3.4. The resulting precipitate was separated by filtration and washed with distilled water. The filtrate was then adjusted to pH 5.0-5.5 to

precipitate aluminium, which was subsequently separated by filtration and washed with distilled water.

After the removal of Fe and Al, the pH of the remaining solution was increased to 9-10 by gradual addition of 40 wt.% KOH solution to recover the manganese-containing solid. The resulting precipitate was separated by filtration, washed repeatedly with distilled water and dried to constant mass before subsequent chemical characterisation.

3. Results and discussion

Some of the preliminary results concerning the characterisation of the investigated material have been reported previously (Dumitrache et al., 2024). However, the present study considerably extends those investigations through a more comprehensive experimental programme that includes detailed mineralogical characterisation, physical separation experiments, hydrometallurgical leaching and subsequent selective precipitation of the dissolved metals, allowing a more complete evaluation of the manganese recovery potential.

3.1. Chemical composition

The initial chemical characterisation of the historical deposit was carried out by X-ray fluorescence (XRF) analysis of the 35 individual samples. The purpose of this stage was to assess the variability in the chemical composition of the deposited material before the subsequent technological investigations.

Table 1 presents the concentration ranges and average values of the main components determined in the 35 samples.

Table 1. Ranges of variation in element concentrations in the 35 analysed samples

Component	Unit	Minimum	Maximum	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
S	%	0.42	1.17	0.77
P	%	0.023	0.051	0.034
Fe	%	2.06	6.04	3.31

The results show considerable variation in the chemical composition across the deposit. The Mn content ranges from 3.64 to 20.47%, with an average value of 15.50%, while the SiO₂ content ranges from 18.88 to 83.54%, with an average value of 35.57%. The wide ranges observed for Mn and SiO₂ indicate the heterogeneous nature of the deposited material and the differences in composition among the sampling locations.

For the subsequent detailed physicochemical characterisation and technological investigations, the representative overall composite sample prepared according to the procedure described in Section 2.2.1 was used. This sample was analysed separately by XRF, and its chemical composition is presented in Table 2.

Table 2. Chemical composition of the representative overall composite sample used in the subsequent investigations

Component	Unit	Content
Mn	%	18.47
SiO ₂	%	35.80
Al ₂ O ₃	%	0.88
S	%	0.75
P	%	0.034
Fe	%	3.35

The composite sample contained 18.47% Mn and 35.80% SiO₂. For the other analysed components, the values determined in the composite sample were close to the average values obtained for the 35 individual samples: 0.88% compared with 0.86% Al₂O₃, 0.75% compared with 0.77% S, 0.034% P in both cases, and 3.35% compared with 3.31% Fe.

The Mn content of the composite sample, 18.47%, was higher than the average value of 15.50% obtained from the 35 individual samples. However, these values represent two different determinations. The value of 15.50% is the average of the individual analyses used to characterise the compositional variability across the deposit, whereas 18.47% was determined directly by XRF analysis of the composite sample used in the subsequent investigations.

The characterised composite sample was used as the feed material for the detailed mineralogical analysis, physical separation tests and hydrometallurgical experiments presented in the following sections.

3.2. Mineralogical analysis

X-ray diffraction (XRD) analysis of the representative composite sample revealed the presence of several manganese-bearing crystalline phases, including birnessite, hausmannite, braunite and jacobsite. These phases contain manganese in different structural environments and oxidation states and therefore show different behaviour during physical separation and hydrometallurgical treatment.

Optical microscopy observations of the representative composite sample (Fig. 2) revealed a heterogeneous morphology consisting of rounded agglomerates of fine particles together with occasional coarse siliceous fragments. The agglomerates contained particles of variable size and appearance, consistent with the heterogeneous character of the material identified by chemical analysis.

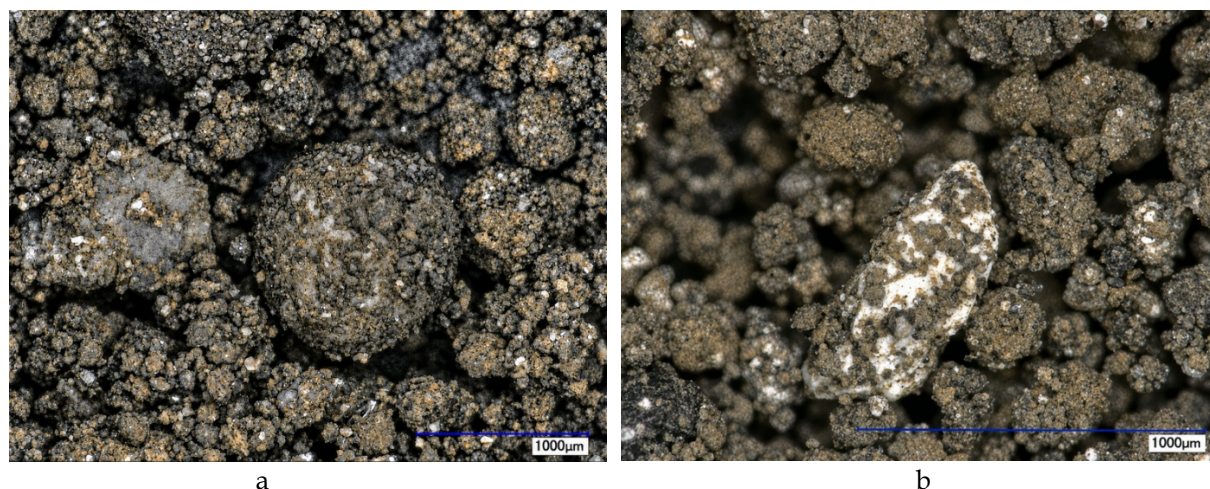


Fig. 2. Optical microscope images of the representative silicomanganese sludge: (a) rounded agglomerates composed of fine particles; (b) coarse siliceous fragment surrounded by fine particles. Scale bar = 1000 µm

The manganese-bearing phases identified by XRD have different magnetic properties. Jacobsite, due to its spinel structure and Fe content, exhibits ferrimagnetic behaviour, while hausmannite may also show magnetic susceptibility. In contrast, birnessite and braunite are less favourable for direct magnetic concentration. The coexistence of phases with different magnetic responses provides a mineralogical explanation for the limited selectivity observed during magnetic separation.

The response of these phases to acid leaching also differs. Birnessite contains manganese in higher oxidation states and can be dissolved under suitable acidic conditions, whereas the more stable structures of hausmannite and particularly the silicate-containing structure of braunite may require more severe leaching conditions. The presence of these different manganese-bearing phases therefore provides a basis for interpreting the effects of leaching medium and temperature observed in the hydrometallurgical experiments (Zhang and Cheng, 2007; Ghafarizadeh et al., 2011; Deer et al., 2013).

Overall, the mineralogical composition indicates why physical separation alone may provide only limited manganese concentration and supports the use of acid leaching as the main recovery stage investigated in this study.

3.3. Results of the particle size analysis

The particle size distribution of the 35 individual samples was determined by dry mechanical sieving. The results showed a relatively consistent distribution of the main particle size fractions, with some variation among the samples. Table 3 summarises the minimum, maximum, and average proportions for each particle size class.

Table 3. Limits of variation in the particle size distribution for the 35 samples

Grain size class (mm)	Minimum (%)	Maximum (%)	Average (%)
>10	0.3	0.7	0.50
10–6.3	1.6	2.3	2.00
6.3–3.15	6.0	7.0	6.51
3.15–2.5	8.5	9.5	9.03
2.5–1.25	27.0	29.0	28.16
1.25–0.5	23.5	25.5	24.34
<0.5	28.0	31.0	29.46

The investigated material was dominated by fine and medium-sized particles. Fractions smaller than 1.25 mm accounted for approximately 54% of the total sample mass, whereas particles larger than 6.3 mm represented approximately 2.5%. The relatively limited variation in particle size distribution among the individual samples indicates that the granulometric characteristics of the deposit were more uniform than its chemical composition.

The representative overall composite sample prepared as described in Section 2.2.1 was subsequently analysed using the same sieving procedure. Table 4 presents its particle size distribution. This sample was used as the feed material for the subsequent physicochemical characterisation and technological investigations.

Table 4. Particle size distribution of the representative overall composite sample

Grain size class (mm)	Content (%)	Mass from 1000 g sample (g)
>10	0.52	5.2
10–6.3	1.98	19.8
6.3–3.15	6.55	65.5
3.15–2.5	9.05	90.5
2.5–1.25	28.10	281.0
1.25–0.5	24.30	243.0
<0.5	29.50	295.0
Total	100.00	1000.0

The particle size distribution of the composite sample was in close agreement with the average distribution obtained for the 35 individual samples. Differences between the corresponding particle size fractions were only 0.02–0.06 percentage points. This close agreement confirms that the composite sample retained the overall granulometric characteristics of the material across the investigated deposit.

3.4. Chemical composition of the particle size fractions

To evaluate the distribution of manganese and associated elements as a function of particle size, the individual particle size fractions obtained by dry sieving of the representative composite sample were

analysed separately by X-ray fluorescence (XRF). Table 5 summarises the chemical composition of the individual particle size fractions.

Table 5. Chemical composition of the particle size fractions (composite sample)

Grain size class (mm)	Mn (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	S (%)	P (%)	Fe (%)
>10	13.66	47.92	0.80	0.70	0.035	3.0
10–6.3	15.38	45.03	0.85	0.72	0.035	3.1
6.3–3.15	16.51	40.01	0.85	0.74	0.034	3.2
3.15–2.5	17.65	35.99	0.86	0.75	0.034	3.3
2.5–1.25	17.99	33.85	0.86	0.77	0.034	3.3
1.25–0.5	18.44	33.12	0.87	0.78	0.034	3.4
<0.5	19.93	31.09	0.90	0.80	0.033	3.5

The results indicate a clear increase in manganese content with decreasing particle size. The Mn content increased from 13.66% in the coarsest fraction (>10 mm) to 19.93% in the finest fraction (<0.5 mm). In contrast, the SiO₂ content decreased from 47.92% to 31.09% over the same particle size range, indicating a relative enrichment of manganese-bearing material in the finer fractions and a higher proportion of siliceous material in the coarser fractions.

Manganese was nevertheless present throughout the entire particle size range, indicating that the manganese-bearing phases were not concentrated exclusively in a single fraction. The difference between the coarsest and finest fractions was approximately 6.3 percentage points Mn, showing that particle size classification produced only moderate enrichment.

When the mass proportions of the particle size fractions were combined with their corresponding Mn concentrations, the reconstructed Mn content of the composite sample was approximately 18.47%, in agreement with the Mn content determined directly by XRF for the representative composite sample. This agreement confirms the internal consistency of the particle size and chemical composition data.

The combined particle size and chemical composition results indicate that finer fractions are moderately enriched in manganese, but a substantial amount of manganese remains distributed across the other size classes. Particle size classification alone is therefore insufficient for efficient manganese recovery and was considered primarily as a characterisation and preliminary pre-concentration step before the subsequent separation and hydrometallurgical investigations.

3.5. Densimetric analysis

Density separation performed using bromoform ($\rho \approx 2.89 \text{ g/cm}^3$) produced two distinct fractions: a heavy fraction (sink) and a light fraction (float). Table 6 summarises the results.

Table 6. Results of the densimetric separation (composite sample)

Parameter	UM	Heavy fraction	Light fraction
Mass fraction	%	17.73	82.27
Mn	%	25.43	16.97
SiO ₂	%	13.31	40.65
Al ₂ O ₃	%	0.68	0.92
S	%	0.44	0.82
P	%	0.05	0.031
Fe	%	3.28	3.37
Mn recovery (%)	%	24.41	75.59

The heavy fraction represented 17.73% of the total sample mass and contained 25.43% Mn, compared with 18.47% Mn in the initial composite sample. This corresponds to an enrichment factor of approximately 1.38. The light fraction represented 82.27% of the sample mass and contained 16.97% Mn, showing that a substantial amount of manganese remained in the lower-density product.

A marked separation of the siliceous component was also observed. The SiO₂ content decreased from 35.80% in the initial composite sample to 13.31% in the heavy fraction, whereas the light fraction contained 40.65% SiO₂. This behaviour indicates preferential concentration of denser manganese-bearing material in the sink fraction and preferential reporting of silica-rich material to the float fraction.

The manganese recovery in the heavy fraction was 24.41%, whereas 75.59% remained in the light fraction. Thus, although the Mn grade increased from 18.47% in the feed to 25.43% in the heavy fraction, only about one quarter of the manganese inventory was recovered in this product. The relatively high Mn content of the light fraction confirms that manganese-bearing particles are not restricted to the high-density fraction.

The manganese mass balance was checked using the mass yields and Mn concentrations of the two separation products. The reconstructed feed grade was 18.47% Mn, in agreement with the Mn content determined directly for the representative composite sample. The corresponding Mn recoveries of 24.41% and 75.59% for the heavy and light fractions, respectively, give an overall manganese balance of approximately 100%.

The observed behaviour is consistent with the mineralogical complexity of the material. Dense Mn-bearing phases can preferentially report to the heavy fraction, whereas the occurrence of manganese in fine particles and in phases associated with the silicate matrix limits complete separation based on density alone. This explains the simultaneous increase in Mn grade and decrease in SiO₂ content in the heavy fraction, together with the substantial amount of manganese remaining in the light fraction.

Density separation therefore provided partial pre-concentration rather than complete manganese recovery. The increase in Mn grade from 18.47% to 25.43% and the decrease in SiO₂ from 35.80% to 13.31% demonstrate the selectivity of the separation, but the recovery of only 24.41% of the manganese in the heavy product shows that density separation alone is insufficient for efficient recovery of manganese from the investigated silicomanganese sludge.

3.6. Magnetic concentration

Magnetic separation is one of the physical methods commonly used in the treatment of metallurgical wastes and is based on differences in the magnetic susceptibility of the constituent mineral phases. In the case of silicomanganese sludge, this method was investigated to evaluate its potential for manganese pre-concentration, considering the occurrence of manganese in phases with different magnetic properties and its association with the siliceous matrix.

Magnetic separation was performed on four particle size fractions obtained by sieving: <0.075 mm, 0.075–1 mm, 1–3.15 mm and >3.15 mm. A laboratory-scale dry magnetic separation setup equipped with a permanent ferrite magnet was used, generating a low-intensity magnetic field of approximately 0.2 T. Each particle size fraction was processed separately, and the resulting magnetic and non-magnetic products were collected and weighed. Their MnO contents were subsequently determined by XRF analysis. The mass yield of the magnetic product and the MnO recovery in the magnetic product were calculated for each particle size fraction. The results are presented in Table 7.

The results show that low-intensity magnetic separation produced only moderate MnO enrichment. The MnO content of the magnetic products ranged from 27.11 to 28.60%, compared with 23.63–24.98%

Table 7. Magnetic separation results for the investigated particle size fractions

Particle size class (mm)	Class mass proportion in feed (%)	Magnetic product mass yield (%)	MnO in magnetic product (%)	MnO in non-magnetic product (%)	MnO in initial fraction (%)	MnO recovery in magnetic product (%)	Contribution to overall Mn recovery (%)
>3.15	9.05	13.04	27.11	23.25	23.63	14.96	1.35
3.15–1	45.15	23.08	27.90	22.80	23.96	26.88	12.14
1–0.075	35.80	21.20	27.45	23.14	24.05	24.20	8.66
<0.075	10.00	46.24	28.60	22.02	24.98	52.94	5.29

in the corresponding initial particle size fractions. Therefore, the increase in MnO content was limited to approximately 3–4 percentage points, indicating that magnetic separation did not produce a strongly enriched manganese concentrate under the investigated conditions.

The coarsest fraction (>3.15 mm) showed the weakest response to magnetic separation. The magnetic product represented only 13.04% of this particle size fraction and contained 27.11% MnO, compared with 23.63% MnO in the initial fraction. The corresponding MnO recovery in the magnetic product was 14.96%. Considering that this particle size class represented 9.05% of the feed, its contribution to the overall Mn recovery was only 1.35%.

A different behaviour was observed for the finest fraction (<0.075 mm), which showed the strongest response to magnetic separation. The magnetic product represented 46.24% of this fraction and contained 28.60% MnO, compared with 24.98% MnO in the initial material. Consequently, the MnO recovery in the magnetic product reached 52.94%, the highest value obtained among the investigated particle size classes.

Despite the high recovery achieved within the <0.075 mm fraction, its contribution to the overall Mn recovery was 5.29%, because this particle size class represented only 10.00% of the feed. In contrast, the 3.15–1 mm fraction provided the largest contribution to overall Mn recovery, reaching 12.14%. Although its within-class MnO recovery was lower (26.88%), this fraction accounted for 45.15% of the feed. The intermediate 1–0.075 mm fraction showed an MnO recovery of 24.20% and contributed 8.66% to the overall recovery.

Considering the contributions of all four particle size fractions, the calculated overall Mn recovery in the combined magnetic products was approximately 27.44%. This result indicates that most of the manganese remained in the non-magnetic products despite the partial enrichment obtained in the magnetic fractions. The limited performance of low-intensity magnetic separation is consistent with the mineralogical complexity of the investigated material, in which manganese occurs in several phases exhibiting different magnetic responses.

Overall, direct low-intensity magnetic separation provides only partial manganese pre-concentration and cannot be considered an efficient standalone recovery method for the investigated silicomanganese sludge. Nevertheless, the preferential recovery observed in some particle size fractions, particularly in the finest fraction, indicates that magnetic separation may have potential as a preliminary physical treatment prior to subsequent hydrometallurgical processing.

3.7. Hydrometallurgical treatment and manganese enrichment

Given the limited manganese recovery achieved by the physical separation methods investigated, hydrometallurgical treatment was evaluated as an alternative approach for manganese recovery. The investigated route consisted of acid leaching followed by alkaline precipitation of manganese from the resulting leach solution. The recovered precipitates were filtered, washed, dried and subsequently analysed by XRF to determine their MnO-equivalent content.

The mineralogical analysis showed that manganese occurs in several phases, including birnessite, hausmannite and braunite, which may exhibit different behaviour in acidic media. Based on these mineralogical characteristics, leaching experiments were performed using HCl-water and aqua regia-water systems. For the HCl-water system, experiments were conducted at 25 and 80 °C. Following leaching, the resulting solution was subjected to alkaline precipitation, and the recovered solid product was analysed by XRF. The results therefore represent the MnO-equivalent content of the recovered precipitate rather than a direct measurement of dissolved manganese in the leach solution. Table 8 presents the results for the HCl-water system.

At 25 °C, the MnO-equivalent content of the recovered precipitate increased from 82.0% for the 25% HCl system to a maximum of 85.2% at an equal volumetric proportion of HCl solution and water. Further increases in the HCl proportion gradually decreased the MnO-equivalent content of the recovered product, reaching 75.4% when the initial HCl solution was used without water addition. Thus, under the investigated conditions at 25 °C, increasing the HCl proportion did not continuously improve the MnO-equivalent content of the recovered precipitate.

A markedly different trend was observed at 80 °C. Under these conditions, the MnO-equivalent content of the recovered precipitate increased progressively with increasing HCl proportion, from

83.9% at 25% HCl to values approaching 100% at the highest HCl proportions. The recovered product contained 99.1% MnO equivalent at 95% HCl, while XRF analysis of the precipitate obtained using the initial HCl solution gave a value of 100.4%. These results indicate that the combination of higher temperature and high HCl proportion favoured the production of a manganese-rich precipitate with a high MnO-equivalent content.

Table 8. XRF-reported MnO-equivalent content in the recovered precipitates obtained from the HCl-water system at 25 and 80 °C

No.	HCl (%)	Water (%)	MnO-equivalent content in the recovered precipitate at 25 °C (%)	MnO-equivalent content in the recovered precipitate at 80 °C (%)
1	100	0	75.4	100.4
2	95	5	76.4	99.1
3	90	10	77.4	97.7
4	85	15	78.3	96.4
5	80	20	79.3	95.0
6	75	25	80.3	93.7
7	70	30	81.3	92.4
8	65	35	82.3	91.0
9	60	40	83.2	89.7
10	55	45	84.2	88.3
11	50	50	85.2	87.0
12	45	55	84.6	86.4
13	40	60	83.9	85.8
14	35	65	83.3	85.1
15	30	70	82.6	84.5
16	25	75	82.0	83.9

At 25 °C, the highest MnO-equivalent content was obtained at an intermediate HCl-water proportion rather than at the highest HCl proportion. This indicates that the composition of the recovered precipitate was influenced by the overall leaching and precipitation conditions rather than solely by the proportion of HCl used. Since the individual effects of manganese dissolution, co-dissolution of other components and subsequent precipitation were not independently quantified, the maximum observed at 50% HCl should primarily be regarded as an experimental trend.

The comparison between the two temperature series nevertheless shows that temperature had a pronounced influence on the composition of the recovered product, particularly at high HCl proportions. For example, when the initial HCl solution was used without water addition, the MnO-equivalent content of the recovered precipitate increased from 75.4% at 25 °C to an XRF-reported value of 100.4% at 80 °C. This indicates that the higher-temperature treatment, combined with the subsequent precipitation step, was favourable for obtaining a manganese-rich product with a high MnO-equivalent content.

Aqua regia was also investigated as a strongly acidic and oxidising leaching medium. After leaching, the resulting solutions were subjected to the same subsequent recovery procedure, and the recovered precipitates were analysed by XRF. Table 9 presents the results obtained at different aqua regia-water proportions.

The aqua regia-water experiments showed an overall increase in the MnO-equivalent content of the recovered precipitate as the proportion of aqua regia increased. The MnO-equivalent content increased from 43.8% at 10% aqua regia to 91.5% at an equal volumetric proportion of aqua regia and water. At aqua regia proportions of 80% and above, the recovered precipitates contained more than 98% MnO equivalent according to XRF analysis. The XRF-reported values of 100.4% and 100.7% should not be interpreted as physical MnO-equivalent content exceeding 100%. These values reflect small positive analytical and normalisation deviations associated with XRF oxide reporting and should therefore be interpreted as approximately 100% MnO equivalent.

Table 9. XRF-reported MnO-equivalent content in the recovered precipitates obtained from the aqua regia-water system

No.	Aqua regia (%)	Water (%)	Temperature (°C)	MnO-equivalent content in the recovered precipitate (%)
1	100	0	38	100.7
2	90	10	43	99.4
3	80	20	47	98.1
4	70	30	48	96.3
5	60	40	45	94.2
6	50	50	41	91.5
7	40	60	37	86.8
8	30	70	33	78.6
9	25	75	31	72.9
10	20	80	30	64.7
11	10	90	27	43.8

An important aspect of the aqua regia experiments is that reagent proportion and operating temperature were not varied independently. As shown in Table 9, temperature changed together with the aqua regia-water proportion. Consequently, the increase in the MnO-equivalent content of the recovered precipitate cannot be attributed exclusively to the increasing proportion of aqua regia. The observed trend reflects the combined effect of the experimental conditions applied during leaching and subsequent recovery, and the individual contributions of reagent proportion and temperature cannot be separated on the basis of the present experimental dataset.

Nevertheless, the results clearly show that high aqua regia proportions under the investigated conditions favoured the formation of manganese-rich precipitates with high MnO-equivalent contents. Values above 90% MnO equivalent were obtained at aqua regia proportions of 50% and above, while the recovered products approached 100% MnO equivalent at the highest reagent proportions investigated.

Fig. 3 provides a comparative representation of the MnO-equivalent content of the recovered precipitates obtained from the HCl-water and aqua regia-water systems.

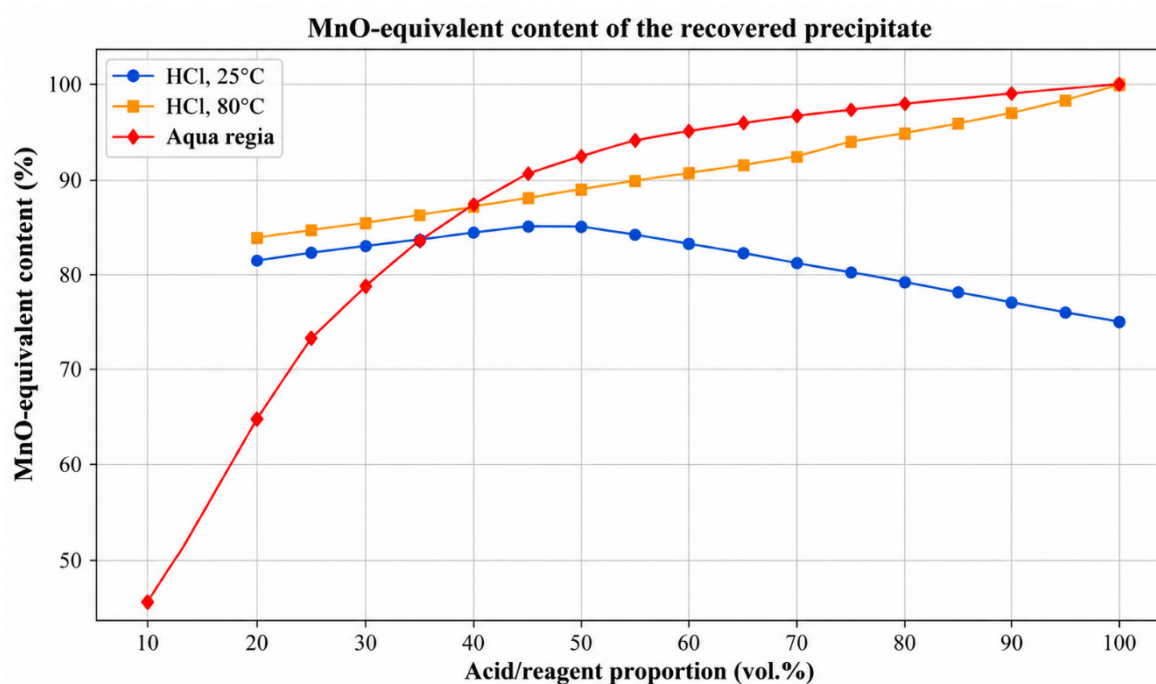


Fig. 3. Effect of reagent proportion and temperature on the MnO-equivalent content of the recovered precipitates in the HCl-water and aqua regia-water systems

The comparative results presented in Fig. 3 highlight the different behaviour of the two investigated systems. For the HCl-water system, where experiments were conducted at two fixed temperatures, the effect of temperature on the composition of the recovered precipitate can be directly compared. At 25 °C, the highest MnO-equivalent content was obtained at an intermediate HCl-water proportion, whereas at 80 °C the MnO-equivalent content of the recovered product increased progressively with increasing HCl proportion and approached 100% at the highest reagent proportions.

For the aqua regia-water system, the MnO-equivalent content of the recovered precipitate also increased markedly across the investigated series, reaching values above 98% at high aqua regia proportions. However, because reagent proportion and temperature varied simultaneously, this trend must be interpreted as the combined response to both experimental variables rather than as an independent effect of aqua regia proportion.

Comparison of the highest values shows that manganese-rich precipitates with high MnO-equivalent contents were obtained using both hydrometallurgical systems. In the HCl-water system, a product approaching 100% MnO equivalent was obtained at 80 °C at the highest HCl proportions, while aqua regia produced comparable MnO-equivalent content at high reagent proportions under the investigated temperature conditions. The results are particularly relevant because they show that a strongly manganese-enriched solid product can also be obtained using HCl, without requiring aqua regia as the leaching medium.

Overall, the hydrometallurgical route combining acid leaching and subsequent precipitation resulted in manganese-rich solid products with high MnO-equivalent contents. In the HCl-water system, precipitates containing more than 90% MnO equivalent were obtained at 80 °C at high HCl proportions, with values approaching 100% under the most favourable conditions. Aqua regia produced similarly manganese-rich precipitates at high reagent proportions. These results demonstrate the potential of the investigated hydrometallurgical route for recovering manganese from silicomanganese sludge as a high-purity manganese-rich product.

3.8. Purification of the leach solution and recovery of the manganese-rich product

Following acid leaching, the resulting solutions were subjected to sequential alkaline precipitation using a 40 wt.% KOH solution. The pH was increased stepwise to promote the selective removal of the main dissolved impurities before manganese recovery. Iron-bearing species were first precipitated at pH 3.2-3.4, followed by aluminium-bearing species at pH 5.0-5.5. After each precipitation step, the solid phase was separated by filtration. The pH of the remaining manganese-containing solution was then increased to approximately 9-10 to recover manganese as a solid precipitate.

The manganese-rich precipitates were filtered, washed with distilled water, dried, and analysed by XRF. Several of the investigated conditions resulted in products containing more than 90% MnO equivalent, and under the most favourable conditions the XRF-reported MnO-equivalent content approached 100%. Representative high-grade precipitates were therefore selected for a more detailed compositional comparison, including the main residual components SiO₂, Fe₂O₃, Al₂O₃, CaO and K₂O, as presented in Table 10.

Table 10 shows that sequential hydrometallurgical treatment produced manganese-rich precipitates with very low concentrations of the main accompanying components. For the HCl-water system, the highest-grade products were obtained at high HCl proportions. At 95% HCl and 80 °C, the precipitate contained 99.1% MnO equivalent, while the residual contents of SiO₂, Fe₂O₃, Al₂O₃, CaO and K₂O were 0.020, 0.081, 0.020, 0.007 and 0.011%, respectively. With undiluted HCl at the same temperature, the XRF-reported MnO equivalent reached 100.4%, while each of the measured accompanying components remained below 0.1%.

A similar trend was observed for the aqua regia-water system. At 90% aqua regia, the recovered precipitate contained 99.4% MnO equivalent, with residual contents of 0.018% SiO₂, 0.087% Fe₂O₃, 0.020% Al₂O₃, 0.007% CaO and 0.010% K₂O. With undiluted aqua regia, the MnO-equivalent value reached 100.7%, while each of the measured accompanying components remained below 0.1%. At a lower reagent proportion, the MnO-equivalent content decreased and higher concentrations of residual components were observed. For example, the product obtained with 80% aqua regia contained 98.1% MnO equivalent, together with 0.220% SiO₂, 0.750% Fe₂O₃ and 0.320% Al₂O₃.

Table 10. XRF composition of representative manganese-rich precipitates obtained under selected hydrometallurgical conditions

Leaching system	Reagent proportion	Temperature (°C)	MnO equivalent (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	CaO (%)	K ₂ O (%)
HCl-water	100% HCl	80	100.4	0.015	0.077	0.018	0.005	0.009
HCl-water	95% HCl	80	99.1	0.020	0.081	0.020	0.007	0.011
HCl-water	90% HCl	80	97.7	0.420	0.650	0.220	0.035	0.200
Aqua regia-water	100% aqua regia	38	100.7	0.014	0.075	0.017	0.005	0.008
Aqua regia-water	90% aqua regia	43	99.4	0.018	0.087	0.020	0.007	0.010
Aqua regia-water	80% aqua regia	47	98.1	0.220	0.75	0.32	0.06	0.12

Note: The XRF-reported values of 100.4% and 100.7% should not be interpreted as physical MnO-equivalent content exceeding 100%. These values reflect small positive analytical and normalisation deviations associated with XRF oxide reporting and should therefore be interpreted as approximately 100% MnO equivalent.

The low Fe₂O₃ and Al₂O₃ contents measured in the highest-grade products are consistent with the effectiveness of the sequential purification procedure. The removal of Fe-bearing species at pH 3.2–3.4 and Al-bearing species at pH 5.0–5.5 prior to manganese precipitation limited the presence of these impurities in the final solid product. The simultaneous reduction of Si-, Fe-, Al-, Ca- and K-bearing components indicates that the proposed treatment not only concentrated manganese but also substantially improved the chemical purity of the recovered precipitate.

The MnO-equivalent values of 100.4% and 100.7% obtained under the most favourable experimental conditions reflect small positive analytical and normalisation deviations associated with XRF oxide reporting and should therefore be interpreted as approximately 100% MnO equivalent.

Overall, acid leaching followed by sequential removal of Fe- and Al-bearing impurities and final alkaline precipitation resulted in a highly purified manganese-rich product. The very low residual concentrations of the principal accompanying components, particularly under the most favourable HCl and aqua regia conditions, demonstrate the effectiveness of the purification stage and confirm that the proposed route extends beyond manganese dissolution to the recovery of a high-grade manganese-rich solid product.

3.9. Comparative evaluation of physical and hydrometallurgical recovery routes

The results obtained from the physical separation experiments and the hydrometallurgical investigations show substantial differences in the behaviour of the investigated silicomanganese sludge under the different recovery approaches. The effectiveness of each method is closely related to the chemical and mineralogical characteristics of the material and to the occurrence of manganese in mineral phases with different physical and chemical properties. Table 11 summarises the separation principles, main advantages, limitations and experimental performance of the investigated methods.

Fig. 4 provides a graphical comparison of the experimental performance of the investigated recovery routes. Magnetic and density separation resulted in Mn recoveries of 27.4% and 24.4%, respectively, whereas the hydrometallurgical treatment produced a manganese-rich precipitate with an MnO-equivalent content of approximately 100% under the most favourable conditions. The

hydrometallurgical value represents the composition of the recovered product rather than a directly equivalent manganese recovery value and should therefore be interpreted accordingly.

Table 11. Comparative evaluation of the physical and hydrometallurgical methods investigated for manganese recovery from silicomanganese sludge

Method	Principle	Main advantages	Main limitations	Results obtained in this study
Particle size classification	Separation according to particle size	Simple method; provides information on manganese distribution among size fractions	Mn occurs throughout the particle size range; limited concentration by size classification alone	Mn increased from 13.66% in the >10 mm fraction to 19.93% in the <0.5 mm fraction
Magnetic separation	Separation according to magnetic susceptibility	Partial concentration of phases with higher magnetic susceptibility	Mn occurs in phases with different magnetic properties; a substantial proportion of Mn remains in the non-magnetic product	Moderate Mn enrichment in the magnetic products; overall Mn recovery in the magnetic product: 27.4%, with the strongest response observed for the finest fraction
Density separation	Separation according to particle density	Produces a Mn-enriched heavy product with lower SiO ₂ content	Most Mn remains in the light product because the heavy product represents a relatively small mass fraction	Heavy product: 25.43% Mn; Mn recovery in the heavy product: 24.41%
Acid leaching followed by alkaline precipitation	Chemical dissolution followed by sequential impurity removal and Mn precipitation	Strong Mn enrichment and substantial removal of major accompanying components	Requires acid and alkali consumption and downstream solid-liquid separation	Representative precipitates contained 97.7-100.7% MnO equivalent, with very low residual impurity contents under the most favourable conditions

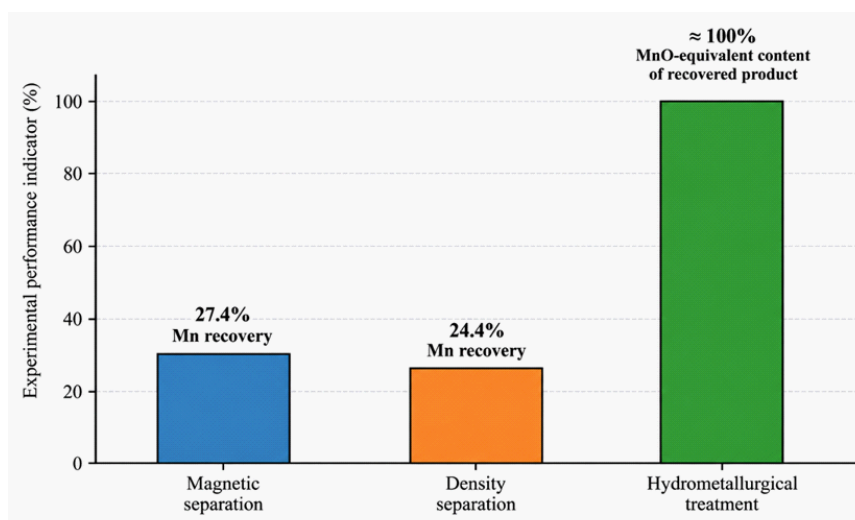


Fig. 4. Comparative performance of the investigated physical and hydrometallurgical recovery methods

Particle size classification showed a gradual increase in manganese content with decreasing particle size, from 13.66% Mn in the >10 mm fraction to 19.93% Mn in the <0.5 mm fraction. However, manganese remained distributed throughout the entire particle size range. Size classification therefore provided only moderate pre-concentration and did not allow selective manganese recovery.

Magnetic separation also resulted in moderate manganese enrichment. This behaviour is consistent with the mineralogical complexity of the material and the occurrence of manganese in phases with different magnetic properties. Although the magnetic products were enriched in manganese relative to the corresponding non-magnetic products, the overall Mn recovery in the magnetic product was 27.4%. The strongest separation response was observed for the finest fraction. A substantial proportion of manganese nevertheless remained in the non-magnetic products, indicating that magnetic separation alone is insufficient for efficient recovery.

Density separation produced a more pronounced enrichment of manganese in the heavy product. The heavy fraction, representing 17.73% of the separated material, contained 25.43% Mn and accounted for 24.41% of the manganese recovery. The accompanying decrease in SiO₂ content indicates preferential concentration of denser manganese-bearing particles. However, 75.59% of the manganese remained in the light product. Density separation can therefore provide useful pre-concentration, but cannot serve as an independent route for efficient manganese recovery.

In contrast to the physical separation methods, hydrometallurgical treatment acted directly on the manganese-bearing phases through acid leaching, followed by sequential purification and alkaline precipitation. The recovered precipitates were strongly enriched in manganese, with representative products containing 97.7-100.7% MnO equivalent. Under the most favourable conditions, the residual contents of the principal accompanying components were generally below 0.1%. These results indicate that hydrometallurgical treatment achieved a substantially higher degree of manganese concentration and impurity removal than the physical methods investigated.

The physical and hydrometallurgical methods should not be compared solely on the basis of a single numerical recovery parameter, because the reported indicators describe different aspects of process performance. For the physical methods, the values refer to manganese distribution and recovery in the separated products, whereas the hydrometallurgical value represents the MnO equivalent content of the manganese-rich precipitate obtained after leaching, purification and precipitation. Fig. 4 should therefore be interpreted as a comparative representation of the experimental performance of the investigated routes rather than as a direct comparison of equivalent manganese recovery values.

The physical and hydrometallurgical methods were evaluated independently in the present study. Physical separation provided partial manganese pre-concentration, whereas acid leaching followed by controlled precipitation produced highly purified manganese-rich products. These results suggest that physical pre-concentration could potentially reduce the amount of material subsequently subjected to chemical processing. However, such an integrated flowsheet was not experimentally investigated in the present work and therefore requires separate experimental validation.

The results further show that the mode of occurrence of manganese in the investigated sludge strongly influences the effectiveness of each recovery route. Its distribution throughout the particle size range and among mineral phases with different magnetic and density properties limits the effectiveness of physical separation. Under the investigated conditions, hydrometallurgical treatment achieved the highest degree of manganese concentration and impurity removal among the methods evaluated.

4. Conclusions

The present study investigated the recovery potential of a historical silicomanganese sludge through chemical and mineralogical characterisation, particle size classification, magnetic and density separation, and hydrometallurgical treatment. The analysis of 35 individual samples confirmed the chemical heterogeneity of the deposit, with Mn contents ranging from 3.64 to 20.47% and SiO₂ contents from 18.88 to 83.54%. The representative composite sample used for the recovery experiments contained 18.47% Mn and 35.80% SiO₂.

Particle size classification showed a limited enrichment of manganese in the finer fractions. The Mn content increased from 13.66% in the >10 mm fraction to 19.93% in the <0.5 mm fraction, while SiO₂ decreased from 47.92 to 31.09%. However, manganese remained distributed throughout the entire

particle size range, indicating that size classification alone cannot provide selective manganese recovery.

The physical separation experiments confirmed the limitations imposed by the heterogeneous mineralogical occurrence of manganese. Low-intensity magnetic separation produced magnetic products containing 27.11-28.60% MnO and an overall Mn recovery of approximately 27.4% in the combined magnetic products. Density separation increased the Mn content from 18.47% in the feed to 25.43% in the heavy fraction and reduced SiO₂ to 13.31%, but only 24.41% of the manganese was recovered in this fraction. These results show that both methods can provide partial pre-concentration, but neither is suitable as a standalone recovery route for the investigated material.

Hydrometallurgical treatment provided substantially greater manganese enrichment than the physical methods. Acid leaching followed by sequential precipitation using KOH produced manganese-rich precipitates whose composition varied with the investigated leaching conditions, including the leaching medium, reagent proportion, and temperature. In the HCl-water system, the MnO-equivalent content of the recovered precipitate reached 99.1% at 95% HCl and 80 °C and approached 100% when undiluted HCl was used at the same temperature. The aqua regia-water system produced comparable high-grade products, with 99.4% MnO equivalent at 90% aqua regia and values approaching 100% at the highest reagent proportion investigated. Values slightly above 100% obtained by XRF are attributed to positive analytical deviations associated with the measurement and normalisation procedure and should be interpreted as approximately 100% MnO equivalent.

Sequential precipitation at controlled pH contributed to the purification of the manganese-rich products. Removal of Fe-bearing species at pH 3.2-3.4 and Al-bearing species at pH 5.0-5.5 before manganese precipitation at pH 9-10 resulted in very low residual concentrations of the principal accompanying components. Under the most favourable HCl and aqua regia conditions, the measured SiO₂, Fe₂O₃, Al₂O₃, CaO and K₂O contents were generally below 0.1%.

Comparison of the investigated routes shows that physical and hydrometallurgical performance cannot be expressed by a directly equivalent numerical parameter. The values obtained by magnetic and density separation describe manganese recovery and distribution between physical products, whereas the hydrometallurgical results describe the MnO equivalent composition and chemical purity of the recovered precipitates. Within these limitations, the experiments demonstrate that physical separation provides only partial manganese pre-concentration, while acid leaching followed by selective purification and precipitation produces substantially more concentrated and chemically purified manganese-rich products.

Among the hydrometallurgical conditions investigated, the HCl-water route is particularly relevant because a manganese-rich product approaching 100% MnO equivalent was obtained at 80 °C without the use of aqua regia. The results therefore support HCl leaching followed by controlled sequential precipitation as a promising route for the valorisation of the investigated historical silicomanganese sludge. Further work should quantify manganese dissolution and overall process recovery through solution-phase analysis, confirm the mineralogical and oxidation-state composition of the recovered manganese product, and evaluate reagent consumption and process optimisation before scale-up.

Acknowledgments

A part of the results reported in this paper were presented at XX Balkan Mineral Processing Congress BMPC 2026 entitled "Hydrometallurgical recovery of high-purity manganese dioxide and associated compounds from silico-manganese production dusts".

References

- DEER, W.A., HOWIE, R.A., ZUSSMAN, J., 2013. *An introduction to the rock-forming minerals*. 3rd ed., Mineralogical Society, London.
- DUMITRACHE, M., TRAIȘĂ, C., LANG, M., 2024. *Preliminary studies on the utilization of silicomanganese slurry*. Min. Rev. 30(S1), 152-157.
- EUROPEAN COMMISSION, JOINT RESEARCH CENTRE, 2017. *Best available techniques (BAT) reference document for the non-ferrous metals industries*. Publications Office of the European Union, Luxembourg.
- GASIK, M. (Ed.), 2013. *Handbook of ferroalloys: Theory and technology*. Butterworth-Heinemann, Oxford.

- GHAFARIZADEH, B., RASHCHI, F., VAHIDI, E., 2011. *Recovery of manganese from electric arc furnace dust of ferromanganese production units by reductive leaching*. Miner. Eng., 24(2), 174–176.
- KERO, I.T., EIDEM, P.A., MA, Y., INDRESAND, H., AARHAUG, T.A., GRÅDAHL, S., 2019. *Airborne emissions from Mn ferroalloy production*. JOM, 71(1), 349–365.
- KIM, B.S., JEONG, S.B., JEONG, M.H., RYU, J.W., 2011. *Upgrading of manganese from waste silicomanganese slag by a mechanical separation process*. Mater. Trans., 52(8), 1705–1708.
- MA, Y., MOOSAVI-KHOONSARI, E., KERO, I.T., TRANELL, G.M., 2018. *Element distribution in the silicomanganese production process*. Metall. Mater. Trans. B, 49(5), 2444–2457.
- NKOSI, S., STEENKAMP, J.D., GROOT, D.R., GOUS, J.P., 2011. *Hydrometallurgical process for the recovery of manganese from pelletized silicomanganese submerged arc furnace dust*. In: Proceedings of the Fray International Symposium, Cancun, Mexico.
- OLSEN, S.E., TANGSTAD, M., 2004. *Silicomanganese production: Process understanding*. In: Proceedings of the Tenth International Ferroalloys Congress (INFACON X), Cape Town, South Africa, 1–4 February 2004, South African Institute of Mining and Metallurgy, Johannesburg, South Africa.
- OLSEN, S.E., TANGSTAD, M., LINDSTAD, T., 2007. *Production of manganese ferroalloys*. Tapir Academic Press, Trondheim, Norway.
- ÖNAL, M.A.R., PANDA, L., KOPPARTHI, P., SINGH, V., VENKATESAN, P., BORRA, C.R., 2021. *Hydrometallurgical production of electrolytic manganese dioxide (EMD) from furnace fines*. Minerals, 11, 712.
- ORDIALES FERNÁNDEZ, M., IGLESIAS, J., FERNÁNDEZ GONZÁLEZ, D., SANCHO-GOROSTIAGA, J., FUENTES, A., VERDEJA, L.F., 2016. *Cold agglomeration of ultrafine oxidized dust (UOD) from ferromanganese and silicomanganese industrial process*. Metals, 6(9), 203.
- SHEN, R., ZHANG, G., DELL'AMICO, M., BROWN, P., OSTROVSKI, O., 2005. *Characterisation of manganese furnace dust and zinc balance in production of manganese alloys*. ISIJ International, 45(9), 1248–1254.
- SHEN, R., ZHANG, G., DELL'AMICO, M., BROWN, P., OSTROVSKI, O., 2007. *A feasibility study of recycling of manganese furnace dust*. In: Proceedings of the Eleventh International Ferroalloys Congress (INFACON XI), New Delhi, India, 507–519.
- WALLIN, M., VOLL BUGTEN, A., TRANELL, G., EKSTROEM, K.E., 2021. *Valorization of SiMn sludge for production of low-phosphorus ferroalloys*. J. Sustain. Metall., 7, 978–984.
- XU, J., MA, G., XU, J., LIU, M., ZHANG, X., ZHENG, D., LI, J., 2025. *Kinetics of isothermal reduction of carbon-containing silicomanganese dust*. Int. J. Miner. Metall. Mater., 32(4), 869–878.
- ZHANG, W., CHENG, C.Y., 2007. *Manganese metallurgy review. Part I: Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide*. Hydrometallurgy, 89(3–4), 137–159.