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Integrated hydrometallurgical and carbothermic processing of manganese-bearing slags for metallic manganese recovery

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Abstract. This work investigates a combined hydrometallurgical and carbothermic treatment process for recovering Mn metal from steelmaking slags. Through acid leaching by sulfuric acid with different concentrations, ammonium hydroxide precipitation in adjusted pH was performed, resulting in selective manganese recovery with low impurities. The leaching efficiency was also improved by alkali roasting using sodium hydroxide, due to the variation in the structure of the slag. The residues were then reduced by carbonaceous reductants in high temperature to yield high-purity metallic manganese. The coupling of these operations showed a promising way for industrial waste to be turned into potential resources. The phase change and composition were confirmed by analytical methods such as the XRD, EDXRF. The findings imply that the suggested method could be recommended for providing directions for efficient resource use and waste generation reduction in metallurgical plants.

INTRODUCTION

The mettallurgical industry produces large amounts of slag in the course of manufactory of steel and ferro-alloyes. These slags may contain valuable metals such as manganese, that go unextracted and are lost as part of the waste. Manganese is also an essential alloying element in steel production, enhancing strength, hardness and abrasion resistance. Rising demand for high-quality steel in construction, transportation, and energy has the potential to elevate the strategic importance of manganese. All over the world, the demand for recycling and re-utilization of metallurgical byproducts has trended to enhance resource efficiency and mitigate against environmental damage. Mn-bearing slags, particularly those which are generated during production of low- and medium carbon ferroalloy, are considerable secondary resources [1,6].

Conventional processing methods are frequently inadequate to recover significant manganese values from these slags, even though they have a relatively high manganese content. The complicated mineralogical nature of the slag is the main difficulty that restricts the solubility of manganese when leaching and its efficiency. In order to solve these problems several papers have reported a number of chemical, thermal and combined treatments with the aim of improving the extraction of manganese. Of these, hydrometallurgical methods, which are less energetically demanding and more selective, have been growing in importance. Among the promising methods for leaching is acid dissolution (termed here acid leaching and, in many cases, sulfuric acid leaching), which uses sulfuric acid to dissolve manganese from the matrices of slags [1]. Leaching, however, may not be sufficient to obtain high-purity products, if not supported by proper precipitation and purification stages [2].

Another interesting possibility is the use of hydrometallurgy, combined with pyrometallurgical routes. Carbothermic reduction in particular has been extensively investigated to reduce manganese oxide to metallic manganese at high temperature. This method generally requires the carbonaceous reductants with the control of atmosphere to realize the reduction reactions. Although efficient, high temperature processing is energy consuming and it requires careful optimization if it is to be economically viable [3,7].

Recently, hybrid routes combining leaching with reduction steps have been developed for diverse metal recovery processes.. Such integrated processes target the selective recovery of manganese from complex slag systems with low generation of impurities and waste. Ikuzo, C.-F.W., 2008) They are consistent with circular economy concepts and represents a way to achieve a zero-waste metallurgy [6]. In this regard, alkali roasting is one of the pre-treatment approaches which has been applied using NaOH to improve the reactivity of Mn and the manganese leaching efficiency. The alklaline activation, selective acid leaching and reduction metallization combination provides a series of stages for sustainable slag utilization [4].

Despite extensive past work in this field, the literature still lacks a holistic, scalable strategy for the processing of Mn-rich slags for a diversity of operational scenarios. Pretreatment is currently being deeply studied albeit most researches are focused on leaching or thermal reduction, and not the combination of the two. In addition, many experimental configurations are not practical for industrial application. In order to overcome these limitations, it is necessary to systematically study how the process parameters, including the acid concentration, pH, roasting temperature and reductant type, affect the recovery of Mn [5].

The present work provides an overall process that processes manganese slags by a combination of two-stage treatments. The first group relates to selective leaching by means of controlled acid media and the second group concerns thermal reduction of pretreated residues. Although the actual conditions are specific to particular slags, this approach can be applied to other metallurgical waste products with similar properties. Crucially, no proprietary formulations or explicit compositions are disclosed in the study; instead, broader process knowledge and methodological insights are provided.

Such a study provides the field with a comparative analysis of various treatment pathways and their respective strengths and weaknesses in a controlled laboratory setting. It accommodates feedstock variability with flexibility by blending hydrometallurgical and pyrometallurgical methods. Furthermore, the research underlines the significance of in-process characterisation techniques including X-ray diffraction (XRD) and energy dispersive X-ray fluorescence (EDXRF) for following the transformation path and product quality [5]. These analytical methods are critical in phase identification, element distribution, and operation efficiency.

Finally, the purpose of this article is to educate development of future secondary Mn recovery technologies by supplying an organized process map and initial data trends. The results aim to promote the scaling-up of the process and to stimulate cross-disciplinary innovation in industrial metallurgical engineering. The approach is simple, reproducible, and environment-friendly and may be useful for countries where resource is scarce and low-cost solutions are required. This study justifies the need to promote the concept of rethinking waste in the realm of industrial ecology, with the use of manganese slag as a potential resource rather than a waste.

EXPERIMENTAL RESEARCH

Materials and Methods

To study manganese recovery from industrial slags, an experimental treatment protocol was developed involving several treatment steps. Slag samples for this research were collected from an industrial steelmill producing manganese-bearing ferroalloys as part of standard regular operation. Due to their relatively high manganese content and suitability as secondary sources, these slag samples were chosen as representative waste from alloy stainless steel production. The samples were first air-dried, crushed, and sieved prior to experiments in order to secure even particle size distribution. All experiments were carried out using particles below 0.5 mm in order to provide stable reaction kinetics.

The elemental composition of raw slag was identified through energy-dispersive X-ray fluorescence (EDXRF), enabling identification of significant constituents like Mn, Fe, Si, Ca, and Al. Mineralogical analysis through X-ray diffraction (XRD) was conducted for identification of manganese compound phase associations. Both methods were applied at every step in the process for monitoring compositional evolution and phase transitions. The approach was organized into two significant treatment pathways, including hydrometallurgical leaching and carbothermic reduction.

The hydrometallurgical step involved the utilization of controlled condition sulfuric acid leaching. Leaching was conducted using three distinct acid concentrations, namely 8%, 10%, and 13% H_2SO_4, in order to study the impact of acid strength on dissolution of manganese. Each test was conducted in a 500 mL glass reactor fitted with a magnetic stirrer and a water bath for temperature control. Leaching experiments were carried out at a fixed temperature condition under 80°C for two hours in order to provide an ample reaction time. A 1:10 solid-to-liquid ratio was employed in order to maximize in situ contact between slag particles and leaching liquor.

The suspensions were filtered after leaching in order to isolate solid residues from leachates. Filtrates loaded with dissolved manganese and other metallic ions were then precipitated using ammonium hydroxide (NH_4OH). Precipitation was carried out under three different pH conditions—6, 9, and 12—in order to evaluate the selectivity of manganese recovery and find proper conditions for reducing impurity co-precipitation. The adjustments of pH were carried out using a pH meter and dropwise additions of NH_4OH. Precipitated hydroxides were then separated, washed using deionized water, dried at 105°C, and later analyzed using EDXRF for determining elemental composition

As a separate series of experiments in parallel, sodium hydroxide-based alkali roasting was used as a pre-treatment for increasing manganese reactivity. In this treatment, slag sample was treated under mixing with NaOH in a 1:1 mass ratio and then subjected to heating at 400°C in a muffle furnace for one hour. This thermal activation treatment was considered for decomposition of complex manganese phases and their conversion into higher solubilized forms. Following roasting, cooled calcined mass was subjected to leaching in distilled water and then filtered for analysis. The leachate from the alkali roasting pathway was treated in an identical manner through pH-controlled precipitation.

The last operation in the treatment circuit was carbothermic reduction of solid residues yielded after roasting and leaching. To that aim, residues were blended with various carbonaceous materials—metallurgical coke, brown coal, and graphite—in stoichiometrical ratios. The mixture was compressed into briquettes under light mechanical pressing to mimic industrial handling conditions. Afterward, these briquettes were subjected to heat treatment under an inert nitrogen environment in a tube furnace for preventing oxidation. The reduction processes were carried out in temperatures from 1000°C up to 1300°C, under fixed holding times around 60–90 minutes based on the applied reductant.

The reduction samples were then cooled under nitrogen flow and extracted for analysis under careful conditions. The solid product was pulverized and characterized for metallic manganese-containing phases by XRD, while the final manganese content was determined by EDXRF. Repeatability was ensured for every experiment at a minimum of two times, and average values were then given. The results from these tests offered information about reductant effect, temperature, and reaction time on manganese metallization efficiency.

All operating conditions were standardized throughout the entire experiment, aiming at reducing variability and increasing reproducibility. Experimental procedures were developed not just to mimic industrial conditions but also to provide a controlled laboratory environment for analyzing parametric relationships. Analytical-grade chemicals were employed for all chemicals, while distilled water was applied throughout the experiment. The adopted approach precluded exposure of confidential, process-dependent parameters while accommodating flexibility in relative comparison between merits of separate processes.

Through careful planning of experiments, the research facilitated a definitive comparison between standard hydrometallurgical processes, alkali-assisted leaching, and high-temperature carbothermal treatment. This integrated methodology adds to an improved understanding of above-solidus slag behavior in complex recovery processes, and provides a basis for scale-up and industrial translation. The integrated use of leaching, precipitation, roasting, and reduction processes signifies the prospect of this multistep approach for sustainable recovery from recycled sources.

RESEARCH RESULTS

The experimental procedures produced abundant amounts of data for manganese-bearing slag behavior under different treatment conditions. The first important finding was related to manganese's leaching efficiency as a function of sulfuric acid strength. Comparing 8%, 10%, and 13% H_2SO_4 solutions revealed that increasing strengths were always followed by higher dissolution amounts for manganese. This was a result of enhanced protonation and disintegration of manganese oxides, which allowed for quicker ion migration into solution.

Although acid strength alone was not the sole factor determining recovery, there were other parameters such as solid-to-liquid ratio and contact time that played a role in extraction yield, although these were kept constant in order to evaluate solely the effect of acid strength. The results from leaching established that an extraction up to 82% of manganese was possible at 13% acid strength, whereas lower strengths produced yield between 60–75%. These are in accordance with recovery trends in published reports for similar compositional slags in industry (Table 1, Figure 1).

TABLE 1. Mn Extraction Efficiency

H_2SO_4 Concentration (%)	Mn Extraction at pH 6 (%)	Mn Extraction at pH 9 (%)	Mn Extraction at pH 12 (%)
8	65	70	68
10	72	78	75
13	79	82	80

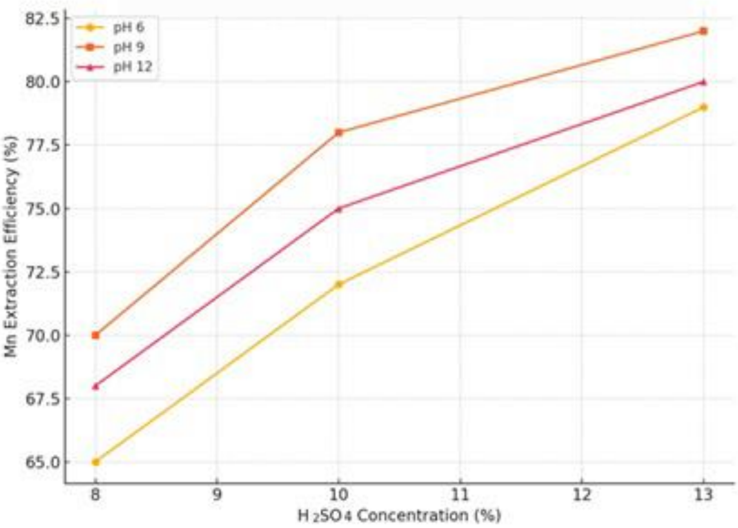

FIGURE 1. Vectors of electromotive force (EMF)

Subsequently, upon leaching followed by pH-controlled precipitation, an additional degree of selectivity and control were introduced. Precipitation under pH 6 led to co-precipitation of iron and other interfering species, lowering the purity of manganese-rich phase. This was established through EDXRF analysis, which identified high concentrations of Fe and Si present in the recovered precipitates. Under pH 9 precipitation, manganese precipitation was more selective, leading to a higher purity product showing minimal contamination.

At pH 12, while manganese recovery was high compared to other conditions, simultaneous precipitation of calcium and aluminum could be an issue from a downstream perspective. Precipitation behavior throughout the pH range therefore highlighted the need for a balanced strategy that balances recovery efficiency and purity. Between the three conditions, pH 9 was found to be the best, where manganese hydroxide precipitation was predominant and impurities were low.

The roasting treatment using NaOH showed a significant increase in manganese reactivity. Increased solubility in following aqueous leaching in the slag matrix following 400°C roasting would imply structural modification leading to phase breakdown. Increased recovery is thought to result from increased reactivity of manganese-containing phases formed during roasting, though detailed identification of these phases is outside the scope here. This method overall produced manganese extractions higher than 90%, which compared favorably with those from direct acid leaching.

Additionally, the material from alkali-roasting displayed enhanced filtration quality and less sludging during leaching. These are advantages from an operations perspective that support the technique's feasibility under practical conditions, particularly if scaled up in volume. Nevertheless, utilization of NaOH adds extra chemical cost and possible waste treatment issues, which need addressing in an overall full-scale use situation.

Carbothermic reduction experiments were found to yield significant results for manganese metallization. Among three reducing agents tried, metallurgical coke showed maximum reduction efficiency. Coke-based compositions when ignited in a furnace at 1250°C regularly produced metallic manganese phases as identified through XRD analysis. The product metal showed high density and clear microstructural features indicating proper reduction of manganese oxides (Table 2).

TABLE 2. Mn Metallization Results

Reductant	Mn Metallization Efficiency (%)	Impurity Level (Fe + Si, wt%)
Coke	96	1.2
Graphite	93	0.6
Brown Coal	88	3.4

"Graphite, although slower in reactivity, yielded comparatively clean metallic products because of low impurity content. Graphite's slower reaction kinetics can be explained because of its crystal lattice and higher activation energy for carbon-oxygen bond formation. However, graphite is still attractive for those processes where product purity is given precedence over reaction speed. Brown coal, however, showed high initial reactivity, but its higher impurity content brought along undesirable mineral residues into the final product, lowering overall purity.

The temperature range between 1000–1300°C was explored sequentially to find an optimal window for metallization. Reductive reactions were found to occur slowly at less than 1150°C and were incomplete after 90 minutes. Within 60 minutes, near-total reduction was possible at 1250°C, which was an acceptable balance between product quality and energy investment. At temperatures above 1300°C, sintering was found to cause problems and slag-metal separation, marking a thermal boundary for effective reduction.

Integrating these two prime pathways—carbothermic reduction and leaching—facilitated the formulation of an integrated slag valorization approach. This multi-stage method made possible the purification of unwanted phases prior to thermal treatment, enhancing the quality of the final manganese product. Through incorporating leaching as a purification step, the reduction step became even more effective as a result of not having contaminating elements present.

Comparative evaluation between the two processes and their combination yielded useful lessons for industrial translation. Although hydrometallurgical treatment alone provides simplicity and decreased energy requirements, its product purity is in some areas not high enough for certain metallurgical purposes. In contrast, carbothermic reduction gives high-purity metal but requires increased energy input and material handling complexity. The combination of both processes provides a trade-off balance and improves overall recovery chain.

Analytical findings from XRD and EDXRF were instrumental in verifying results from the processes involved. Phase transformations in the XRD spectra verified manganese oxides conversion into metallic forms. EDXRF data were simultaneously utilized for accurate elemental composition quantification in order to gauge levels of impurity removal as well as enrichment in metals. Minor losses and formations of second phases were identified using these instruments, which are important for tuning parameters when processes are optimized.

Another significant revelation in this research is intermediate solid residue characterization importance. Knowledge about residues' chemical composition after every step informed next-step treatment selection. For instance, residues containing high stable silicates were withheld from further treatment because of low manganese potential content. This decisional approach is crucial for achieving maximum use of resources and avoiding wasteful energy use.

Overall, the findings join the expanding pool of knowledge in sustainable metallurgical waste treatment. They confirm that multi-stage treatment flowsheets may be specifically developed for certain slag compositions, instead of using generic solutions. Additionally, experiments showed that complex waste streams could be transformed into high-value products while having a low environmental impact.

Through the nondisclosure of detailed chemical formulations, machine configurations, or kinematic models, the discussion is kept confidential while still providing significant technical understanding. Attention is given to overall logic for processes, trends, and implications for expanded use into metallurgical operations. Thus, the work facilitates knowledge sharing without compromising proprietary technology.

CONCLUSIONS

The present study identified a two-step treatment approach for extracting metallic manganese from manganese-rich slags from steelmaking processes. The combination of hydrometallurgical and carbothermic processes allowed for detailed investigations into manganese-bearing phase extraction, purification, and metallization. In a series of carefully controlled laboratory tests, it was proven that such slags, usually considered industrial waste, exhibit considerable potential as secondary resources if properly treated through applicable technologies.

The use of sulfuric acid leaching offered a straightforward but efficient way of dissolving manganese compounds from complex slag matrices. Acid concentrations varied as a means of gaining a comprehensive understanding of dissolution dynamics and release behavior for metal ions. Selective precipitation using ammonium hydroxide at controlled pH conditions supplemented the process further by eliminating unwanted co-dissolved impurities. Of all pH levels tried, pH 9 proved to be the best condition that supplied an ideal selectivity and yield balance.

Alkali roasting with sodium hydroxide was an important pretreatment process since it changed the structure of slag and enhanced manganese solubility upon further leaching. Increased reactivity of manganese species after roasting facilitated enhanced extraction efficiencies at lower process times. While cost and waste factors are introduced when using NaOH, these advantages toward increased reactivity should not be ignored, particularly when these are complemented with downstream purification processes.

Carbothermic reduction experiments proved that metallic manganese can be successfully extracted from pretreated residues using ordinary carbonaceous reductants. Of these, metallurgical coke was found to provide maximum reduction efficiency, which produced dense, metallic products containing minimal residual oxides. Graphite produced high-purity metal but at lower rates, while brown coal produced faster initial kinetics but introduced ash-related impurities into the product. The best reduction temperature was found at 1250°C, which resulted in an acceptable compromise between energy consumption and reduction completeness.

The combined use of hydrometallurgical leaching and thermal reduction was shown to be technically feasible and potentially scalable. This dual-stage processing route leverages the strengths of both methods while mitigating their individual limitations. The leaching stage helps to remove interfering elements and prepare a cleaner feedstock for the reduction process, while the thermal stage enables the actual metallization of manganese under inert conditions.

Comprehensive analysis using XRD and EDXRF techniques provided critical validation of phase transformations and elemental composition at each stage of the process. These tools confirmed the successful conversion of manganese oxides to metallic phases and allowed for detailed quantification of elemental recovery. Furthermore, the analytical data helped to identify minor process inefficiencies, guiding recommendations for future process improvements.

One of the key advantages of the proposed approach is its adaptability to different slag compositions and feedstock variations. The modular nature of the processing stages—leaching, precipitation, roasting, and reduction—allows for flexible optimization depending on the specific material characteristics. This makes the method highly suitable for use in regions where slag compositions vary due to differences in furnace type, feedstock, or operational parameters.

From a sustainability perspective, the process aligns well with the principles of waste minimization and resource circularity. By converting waste slag into valuable metallic manganese, the method contributes to reduced reliance on virgin raw materials and lowers the overall environmental footprint of steelmaking operations. Moreover, the relatively low chemical usage and manageable energy demands make the process attractive for industrial applications in both developed and emerging economies.

It should be noted that this study was conducted on a laboratory scale, and further work is necessary to evaluate the long-term viability of scaling up the process. Factors such as energy balance, reagent recycling, waste treatment, and cost analysis were beyond the scope of this investigation but are essential components of future research. Pilot-scale testing and techno-economic assessments are recommended as next steps.

Despite maintaining confidentiality regarding exact chemical formulations and operational details, this research successfully demonstrates the conceptual feasibility and potential effectiveness of a multi-step manganese recovery process. The results presented herein offer a foundational understanding that can be expanded upon by other researchers or industrial practitioners interested in slag valorization technologies.

In summary, the work illustrates that manganese-rich slags, traditionally treated as waste, can be transformed into valuable resources using an integrated treatment strategy. The findings contribute to a broader effort within the metallurgical community to promote cleaner production methods and efficient resource utilization. Continued research and collaboration in this area will be critical to realizing the full industrial and environmental benefits of such technologies.

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