

# Preparation and Usage of High Quality Manganese-Containing Materials from Ferroalloy Production Waste

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**Keywords:** ferroalloy production waste, aluminothermic method, dope steel, method of enriching ferroalloy

**Abstract.** We propose a flow diagram for processing ferroalloy production waste, such as silicothermic slag from manganese metal, as well as wet and dry powder of cleaning gas from ferroalloy furnaces that smelt manganese alloys.

We experimentally determined the parameters for intensifying the calcium chloride method of enriching ferroalloy production waste, which resulted in a manganese extraction rate of 78-86%, with high-quality manganese concentrates.

We present the results of studies related to the use of high-quality concentrates to dope steel with manganese, when processing it in a bucket, and smelting manganese metal via the aluminothermic method.

## Introduction

Ferroalloy production is a major source of waste such as dump slag and powder-gas emissions. Slag multiplicity ranges from 0.8 to 2.0-2.5 in the production of manganese alloys. The waste slag contains 10-20% manganese.

The greatest number of powder-gas discharges is created from carbon thermal processes. The resulting flue gasses contain 70-90% carbon monoxide and a large amount of fine dust. Thus, when producing 1 tonne of silicomanganese or ferromanganese, the exit gas is 900-1000 m<sup>3</sup>, containing 20-30 g/m<sup>3</sup> of dust, 30-35% of which is MnO.

In global practice, we can isolate three different approaches to solving the issue of extracting metals from mineral technogenic raw materials:

- mechanical; grinding the material with the extraction of components in accordance with their density, magnetic, and other properties;
- pyrometallurgical; firing the material with division between boiling temperature, with subsequent chemical and metallurgical processing;
- hydrometallurgical; processing the material using acid or alkaline solutions, and transferring the extracted components into a solution with subsequent removal of the desired components by extraction or ion exchange.

Many researchers have studied the process of extracting manganese from oxide and carbonate materials containing this element [1-6].

The authors of References [1-4] used sulfur-containing compounds to extract manganese into a solution. One option for processing manganese-containing raw materials is hydrometallurgical processing using sulfur dioxide [2]. At the same time, sulfur dioxide can effectively transfer manganese into a solution by forming soluble MnS<sub>2</sub>O<sub>6</sub> and MnSO<sub>4</sub>. However, when implementing this process, the leaching was complicated by the formation of manganese dithionate and calcium sulfate, deposits of which create difficulties when operating the equipment.

Processing manganese ore using sulfuric acid eliminates the need for sulfur oxides. For mixed oxide carbonates and iron-manganese ores, leaching is carried out in the presence of reductants at atmospheric pressure [3] or in an autoclave [1].

Possible reductants include sulfur dioxide [3], and organic compounds such as glycol [3], and glycerin [4].

The authors of References [6,8] show the necessity of cleaning the solutions given sulfuric acid leaching before the deposition of manganese, due to the high rate at which iron and phosphorous transfer into the solution, which complicates the technology.

A number of authors [6,8,9] used chlorides  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ ,  $\text{FeCl}_2$  in order to extract the manganese into the solution. When ammonium chloride, the manganese ore enrichment technology involves mixing the ore with ammonium chloride, grinding the mixture using balls, exposing it in a tube furnace at  $450\text{ }^\circ\text{C}$  for one hour, and then leaching with hot water to obtain  $\text{MnCl}_2$ . After precipitating the manganese using ammonium chloride solution, the ammonia evaporates and can be reused. In this case manganese extraction can reach 90%. It should be noted that the removal of ammonium chloride in the form of marketable salt by evaporation and crystallization, requires large capital expenditures.

In order to extract manganese from the waste of manganese alloy production, the authors of Reference [9] used calcium chloride.

Using calcium chloride in the extraction of manganese into a solution, is based on exchange reactions



At the first stage, the finely ground material is treated at a temperature of 493-513 K by saturated calcium chloride solution, and at the second stage the solution is treated using limewater, after separating the sludge. In order to obtain the concentrate, the precipitate is calcined.

The advantage of this method lies in the fact that during the leaching of manganese, only one reagent is consumed: the readily available lime. The calcium chloride is regenerated. Another advantage of this method is that the harmful impurities of manganese-containing materials, such as phosphorus, sulfur, and silicon dioxide compounds are insoluble in saturated calcium chloride solution. Therefore, a complicated process such as cleaning the solution from contaminants, is not required.

However, when using this method with calcium chloride, only manganese carbonates have a reaction. Other compounds involving manganese, such as oxides and silicates:  $\text{MnSiO}_3$  and  $\text{Mn}_2\text{SiO}_5$ , do not react with calcium chloride.

Experimental studies of how pure manganese oxides dissolve in saturated solutions of calcium chloride when other chlorides are introduced into the solvent, show that adding ferric chloride allows for the use of the calcium chloride method to dissolve all manganese oxides. At high concentrations of ferric chloride (29.6 % wt.) virtually all extraction of manganese from the oxides is due to the deposition of iron oxide in the precipitate  $\text{Fe}_2\text{O}_3$ , which confirms the X-ray analysis. For these reasons, the dissolution of both  $\text{MnO}$  and  $\text{Mn}_2\text{O}_3$ , as well as  $\text{MnO}_2$  and  $\text{Mn(OH)}_2$  in saturated  $\text{FeCl}_2$  solution, goes almost to the end. As an example, it should be noted that adding  $\text{FeCl}_2$  in the amount of 9.6% into calcium chloride allows us to almost completely dissolve  $\text{MnO}_2$  and about 76% of  $\text{MnO}$  [10,11].

The goal of this study was to investigate the technological parameters involved in extracting valuable manganese from the production waste of dump slag, as well as wet and powder gas cleaning sludge, thereby reducing the adverse environmental impact of this waste, and recycle it almost completely.

## The Experiment

In order to study the possibility of extracting manganese from industrial waste using calcium chloride processes, we used materials having compositions listed in Table 1.

Research was conducted on a multi-chamber autoclave MKA-8-75, with a simultaneously installed set of 8 autoclaves of  $75\text{ cm}^3$  each. The autoclaves were secured in a metal frame that rotated in order to mix the solution in a muffle furnace at a rate of 80 rpm.

Saturated calcium chloride solution was used for leaching purposes, which was prepared using technical  $\text{CaCl}_2$  with close to 96.6%  $\text{CaCl}_2$ . The aqueous solution of  $\text{FeCl}_2$  was prepared by dissolving soft iron in hydrochloric acid. The experimental procedure was as follows: the sample of the dissolvable material (usually 7 grams) was loaded into an autoclave, the solvent was poured in ( $50\text{-}65\text{ cm}^3$ ), the autoclave was closed and fastened in the rotating frame, and the chamber temperature was raised to a predetermined value. The duration of the exposure started when the set temperature was attained.

Table 1- Chemical composition of manganese-containing materials

Name	Chemical composition, wt. %						
	Mn	$\text{Fe}_2\text{O}_3$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	MgO	$\text{P}_2\text{O}_5$
Wet gas cleaning sludge	32.7	3.9	28.6	3.4	2.8	1.13	0.60
Manganese metal slag	18,0	insoluble	30,00	5.00	38.00	5.00	insoluble
Dust from dry gas purification of silico-manganese production	32.5	2.7	29.2	insoluble	4.59	insoluble	0.34

After concluding the experiment, the autoclaves were removed from the chamber and cooled to a temperature of about 353-363 K. After cooling, the solution was filtered, and the residue was washed and dried at 378 K, and analyzed. Manganese extraction was evaluated according to manganese content in the solid residue, and its mass.

In order to process the steel, briquettes were prepared in the ladle, which included the manganese concentrate derived from the production waste (% wt.: 64.0 Mn, 0.5  $\text{SiO}_2$ , 0.002 P, 0.2 Fe), and fine dust from exhaust systems, obtained by fractionation of ferrosilicon FS75, as a reducing agent. The fractionated ferrosilicon was produced using mechanical disruption of the ingots, with subsequent sieving of the shredded mass, thereby forming a large number of small waste products: dust with particle sizes of 1 mm, capturable by suction units, and silt fractions with particle sizes of 3 mm, formed by reseeded of the details 0-15 mm. The number of small waste products was 3-5% of the weight of the processed lumpy ferrosilicon. The silicon content in the small waste ranges from 75-83%. These materials are not applied in the deoxidation and alloying of steel in their initial state.

Dolomite and ash brown coal were used as flux in the briquettes, which are used as fuel in thermal power plants. The ash composition is as follows, % wt.: 8.88  $\text{Al}_2\text{O}_3$ , 23.98  $\text{SiO}_2$ , 0.56  $\text{TiO}_2$ , 45.85 CaO, 4.98 MgO, 6.32 FeO, 8.18  $\text{Fe}_2\text{O}_3$ , LOI – 1.82. When using the dolomite as a binder in the briquettes, we used liquid glass and when using ash, the charge was moistened with water. The finished briquettes were exposed to air for 3-5 days in order to obtain sufficient durability. The fact is that oxides CaO,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  that are present in the ash, react with water to form stable compounds:  $2\text{CaO}$ ,  $\text{SiO}_2, 4\text{H}_2\text{O}$ ,  $3\text{CaO}$ ,  $\text{Al}_2\text{O}_3, 6\text{H}_2\text{O}$ ,  $\text{SiO}_2, 2\text{H}_2\text{O}$ . These compounds have cementing properties. Consequently, ash with the given composition is not only a flux but a binder.

In order to determine the optimal composition of the briquette, we conducted experiments on the Tamman stove.

The briquettes were loaded into the stove heated to 1823-1873 K, and exposed for 3-5 minutes. Each experiment was repeated 3-4 times. The products of the experiment were weighted and analyzed. The extraction of manganese concentrate was used as the optimization parameter.

The study of the treatment process of the steel in the ladle was conducted in lab and industrial environments. In lab tests, the steel was melted in an induction furnace IST-006. The mass of the briquettes used to dope the steel was calculated from the condition that 100% of the manganese from the concentrate would be recovered and assimilated with the steel. Up to 50% of the briquette was loaded into bottom of the ladle, and the rest was set in the metal stream during the release. The batch was completed after 60% of the metal was released from the oven. Metal and slag samples were collected from the furnace and the ladle, and analyzed.

Industrial tests pertaining to processing the steel in the ladle using manganese-containing materials were carried out with smelting the steel in an electric arc furnace with a capacity of 6 tonnes. Three batches of mixtures were made for direct doping.

The first batch is made of briquettes with a diameter of 80 mm and a height of 60-70 mm. The weight of the briquettes varied between 500-600 g. TPP ash and water were used as a binder. The second batch was pelletized on a plate granulator. The yield of pellets larger than 20 mm was 90%. The ratios of the charge components in the briquettes and the pellets were as follows: manganese concentrate (CEC)- 43%, ferrosilicon dust FS75 (75.65%, Si, 2.1 % Al)- 17.4%, dolomite-11.5 %, ash (8.88 %  $\text{Al}_2\text{O}_3$ , 23.98 %  $\text{SiO}_2$ , 0.56 %  $\text{TiO}_2$ , 45.85 %  $\text{CaO}$ , 4.98 %  $\text{MgO}$ , 6.32 %  $\text{FeO}$ , 8.18 %  $\text{Fe}_2\text{O}_3$ , 1.82 % LOI ) – 23.2 %, and water was the rest.

35 L and 45 L steel was smelted in the ladle, using direct alloying technology. The alloying and deoxidation of steel in the ladle were carried out according to the following techniques. Before releasing the metal to the bottom of the ladle, 1/3 of the briquettes (pellets) were released, and the rest were deposited on the metal stream during the release. The steel temperature before the release was 1848 K, and the length of the steel release was 3 minutes. During the melt, samples of the metal and the slag were selected for chemical analysis before the release from the ladle and during the casting.

## Results and Discussion

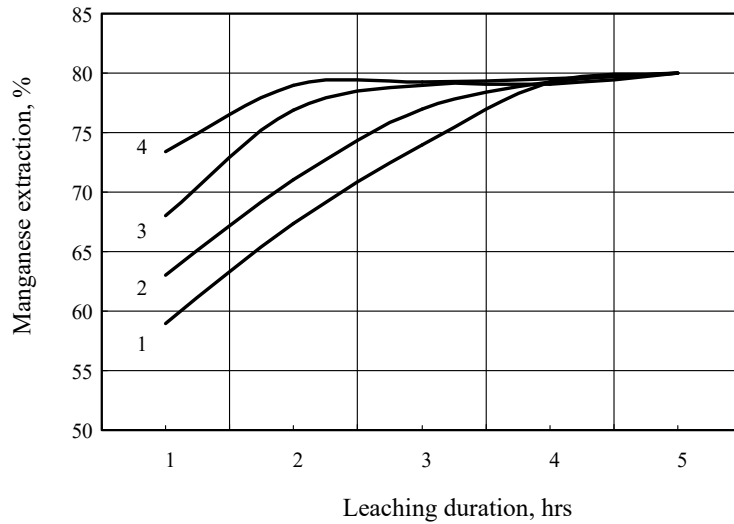
The results of extracting manganese from industrial wastes of manganese alloys and wet and dry gas-cleaning ferroalloy furnaces used to smelt manganese alloys, were obtained using pressure leaching, and are given in Table 2 and Figure 1.

Table 2 shows that the recovery of manganese from the waste under optimal conditions can reach 78-86%.

Figure 1 shows data as to the way temperature and duration of the process affect the extraction of manganese from the wet gas cleaning sludge, given autoclave leaching using a saturated solution of calcium chloride with 4.8% wt. of ferric chloride.

Table 2 - Shows the results of treating wet and dry gas cleaning sludge and waste slag

Name of material	Solvent	Test conditions				Extraction of Mn, %
		Concentration		Temperature, K	Time, hours	
		Solvent wt. %	impurities			
Wet gas cleaning slurry	$\text{CaCl}_2$	41.7	2.6 % $\text{FeCl}_2$	2493	2	65.3
	$\text{CaCl}_2$	40.9	4.8 % $\text{FeCl}_2$	2493	2	78.0
Manganese metal slag	$\text{CaCl}_2$	41.7	2.6 % $\text{FeCl}_2$	2493	2	62.9
	$\text{CaCl}_2$	40.9	4.8 % $\text{FeCl}_2$	2493	2	86.3
Dry gas cleaning dust, from silicomanganese production	$\text{CaCl}_2$	40.9	4.8 % $\text{FeCl}_2$	2493	2	80.3



leaching temperature: 1 – 453 K; 2 – 473 K; 3 – 493 K; 4 – 513 K

Figure 1 - Effects of leaching duration and temperature on the extraction of manganese from wet gas cleaning sludge

It follows from these results that at temperatures less than 493 K, manganese extraction decreases, and at a process temperature above 493 K, the figure is practically unchanged. The highest recoveries of manganese from the processed material are achieved at a leaching duration of 2-2.5 hours.

The research allowed us to find technological methods for extracting manganese from industrial wastes (sludge, slag, dust) to determine the optimum process parameters: duration and temperature of the process, as well as solvent composition.

Based on the obtained results, we proposed an effective technology for recycling the production waste of manganese alloys, wet sludge and dry gas-cleaning dust of ferroalloy furnaces used for smelting manganese alloys (Figure 2).

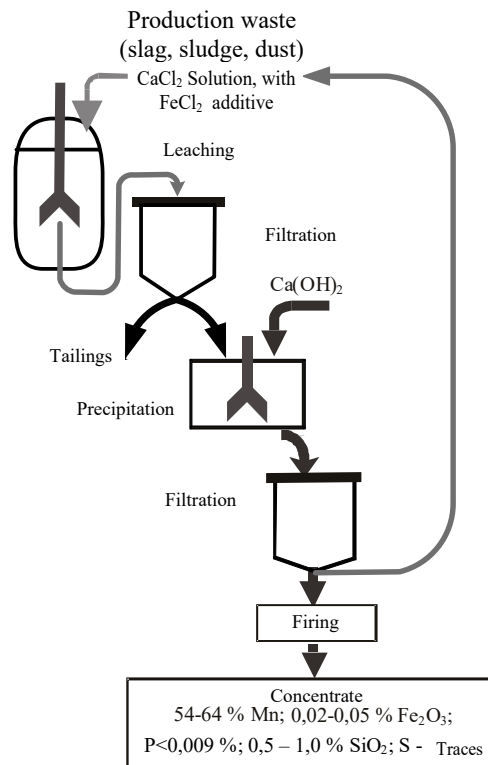


Figure 2 - Shows a diagram of enriching manganese alloy production waste

The flow chart includes grinding the raw material, the preparation of the leach solution ( $\text{CaCl}_2$  and  $\text{FeCl}_2$ ) manganese precipitation [ $\text{Ca}(\text{OH})_2$ ], pressure leaching, and filtration, in which the solution facilitates manganese precipitation and the tails are the raw material for cement production. After precipitation of the manganese, the precipitate is filtered and calcined. As a result, we obtain a high-quality manganese concentrate. The resulting solution of calcium chloride is returned to the technological process.

The obtained concentrate contains wt. %: 58-64 manganese, less than 0.01 phosphorus, 0.02-0.05 iron oxide, 0.5-1.0% silica and traces of sulfur.

Including the enrichment and production of manganese alloys using the developed technologies for manganese extraction from industrial wastes into the technological scheme, allows us to make the whole process virtually waste-free.

In order to produce standard manganese alloys, we must have high-quality manganese-containing raw materials [12-16], but the resulting concentrate is not suitable for smelting alloys using traditional technologies, i.e. it has a low silica content. This is associated with the fact given low silica content, slag formation is absent, as a result of which manganese is lost to evaporation.

It is expedient to use a high-quality concentrate to alloy steel with manganese when processing it in the ladle, the ladle-furnace aggregate, or electric furnace unit [17].

The results of the experiments used to determine the optimal composition of the briquettes showed (Table 3) that when using briquettes with the composition wt. %:

ferrosilicon dust (75-76 % Si)- 46.5-50; manganese concentrate- 38.5-35.5; dolomite -10.5-10; binder-the rest, yields a manganese extraction of 86-88%.

Table 3 - Results of recovering briquette components

Indicators	Experiment series			
	I	II	III	IV
Briquette composition %:				
ferrosilicon dust (75.65 % Si)	41.5	46.5	50	54
manganese concentrate (CEC)	41.5	38.5	35.5	30
dolomite	12	10.5	10	8
binder	5.0	4.5	4.5	2.0
Extraction of manganese concentrate, wt. %	83	88	86	78

Briquettes (Series II) were used for alloying steel in the ladle using silicon and manganese. The steel was melted in an induction furnace with a capacity of 60 kg. The manganese content in the metal discharged from the furnace was 0.10-0.23 wt.%, in the ladle, after adding the briquettes and their dissolution- 0.65-0.75 wt. %, which corresponds to 85-90% of its removal from the concentrate, which is significantly greater than the conventional rates of manganese extraction by doping with standard ferroalloys. Useful use of silicon was 78-89% (Table 4).

Table 4 - Shows the results of deoxidation and alloying the steel by manganese-containing briquettes in an induction furnace

Characteristics	Element contents in the steel, %					
	Mn	Si	Mn	Si	Mn	Si
	Series 1		Series 2		Series 3	
Before doping	0.19	0.27	0.23	0.35	0.10	0.32
After doping	0.78	0.43	0.75	0.50	0.65	0.47
Manganese extraction in the steel, %	90.0		84.73		85.42	

Using the briquettes and pellets for the deoxidation and alloying of the steel (grades St 35 and St 45) in the ladle, as it is smelted in another electric arc furnace, has shown that the dissolution of the briquettes was observed after they were released in the ladle for 30-40 seconds, and that the pellets had time to react during the metal tapping. The reduction in the metal temperature during the release was at the level of conventional melts. "Clot formation" in the metal was not observed.

The technological characteristics of the experimental batches using briquettes and pellets are shown in Table 5.

Table 5 - Technological characterization of the experimental batches

Element contents in the steel, %	Steel grade			
	Conventional melts	Experimental batch		
		St 45L (10 melts on average)	St35L (5 melts on average)	St45L (3 melts on average)
1	2	3	4	5
Before release				
C		0.38	0.44	0.41
Mn		0.29	0.40	0.38
S		0.024	0.023	0.022
P		0.022	0.023	0.020
Si		0.20	0.30	0.19
Al		-	0.006	0.21
In finished steel				
C	0.45	0.37	0.45	0.46
Mn	0.60	0.54	0.62	0.60
S	0.020	0.025	0.024	0.020
P	0.025	0.024	0.024	0.020
Si	0.40	0.27	0.47	0.41
Al	-	-	0.012	0.068
Consumption of deoxidizing and alloying agents, kg				
Into the furnace				
FS65	36	20	25	25
FS75	22	9.8	9.8	9.8
FMn70	15	-	-	-
Into the ladle				
Al	15	15	15	15
Briquettes	-	39	35	39.5
Tap weight, t	4.5	4.5	4.5	4.5
Mn % Extraction	70.0	86.0	88.12	80.88
* - pellets released into the ladle				

## Conclusion

POX technology with the use of an aqueous solution of calcium chloride, with the addition of 4.8% ferric chloride as a solvent, allows us to extract at least 72-85% of manganese from slag, dusts, and sludges, thereby obtaining high-quality manganese concentrates.

The use of manganese briquettes with high-quality manganese concentrate obtained from the industrial waste created by the production of manganese alloys, allows us the possibility of smelting high-quality steel with a low and ultra-low content of phosphorus and sulfur.

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