

Original Research

**UTILIZATION OF A PRODUCT FROM SULFURIC ACID PRODUCTION,
POLLUTING THE ENVIRONMENT, WITH APPLICATION IN FERROUS
METALLURGY**

DOI: 10.5937/EcoTER26353P

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Abstract

In our country works considerable plants for sulphuric acid production, which generate considerable quantities of discarded vanadium catalyst which pollutes the environment. In that time, an ore deposit Obrochiste in Republic of Bulgaria contains a lot of reserves of carbonate manganese ore. The effective utilization on this ore defies a research interest for a long time. Processing of both materials in electrothermal furnace exact agglomeration to suitable sizes and decarbonatization of the ore. This creates an opportunity to utilize a polluting product. It is supposed that the most suitable method for common agglomeration is the sinter process. The aim of this development is to establish the main physical parameters of the process on laboratory sintering in laboratory sinter cup of carbonate manganese ore and waste vanadium catalyst. For preliminarily modeling of the process was used the specific calculation program. It was made qualitative and quantitative characteristic of received sinter from point of view for further thermal manufacturing.

Keywords: waste vanadium catalyst, carbonate manganese ore, sinter.

INTRODUCTION

The complex receiving of elements from carbonate manganese ore and waste vanadium catalyst with heat metallurgical method is not effective to direct manufacturing of raw materials. It is necessary to be joint agglomerated this materials. Attempt for joint agglomeration and sintering of starting raw materials is doing for the first try in department Metallurgy of ferrous metals by UCTM Sofia [1].

For modeling of joint agglomeration is using a modified variant of calculated program Agloprice. Raw materials for the sinter are: coke breeze, manganese concentrate and waste catalyst [1]. A flux material was not use.

After the expert analysis of the receiving results from different variants and with view for the effective of the next heat metallurgical manufacturing of sinter, i. e. to introduce sufficiency quantity of Mn in alloy from maximum drawing out of V and optimal quantity of Si, Al, Ca and Fe. On this way are select compositions of raw materials for laboratory

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agglomeration. The most suitable for this experiment are starting materials with 80, 70 and 60 % manganese concentrate and 20, 30 and 40 % vanadium catalyst [1].

MATERIALS AND METHODS

Installation for sinter

The laboratory agglomeration of manganese concentrate and vanadium catalyst is going on in laboratory sinter cup, Figure 1. The cup is a truncated pyramid which upper and lower radius have quadratic a vertical section. The lower radius is 150 mm and the upper size – 160 mm. The effective height of raw materials is 300 mm. The calculated effective worked volume of the sinter cup is 7,21 dm³ [2].

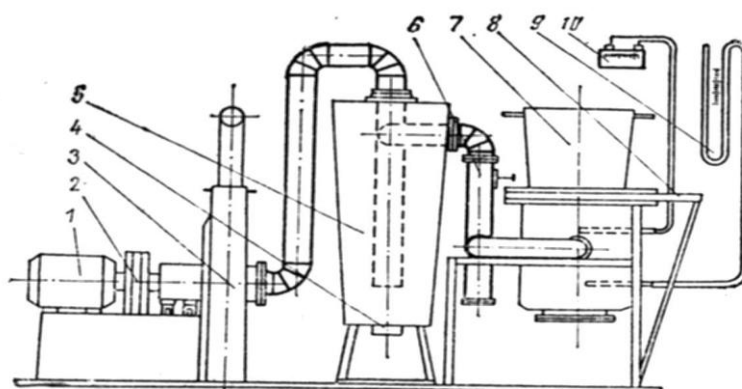


Figure 1 Scheme of laboratory sinter installation: 1 – electrical motor; 2 – connector; 3 – vacuum system; 4 – outlet for cleaning of dust filter; 5 – dust filter; 6 – shutter; 7 – sinter cup; 8 – base; 9 – manometer; 10 – voltmeter

Chemical composition

The chemical composition of the used raw materials is shown in Table 1 [3–5].

Table 1 Chemical composition of raw materials

Chemical composition of waste vanadium catalyst, %									
V ₂ O ₅	Fe ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O	Al ₂ O ₃	SO ₃			
4,12	3,40	57,12	6,71	3,93	0,82	23,88			
Chemical composition of coke breeze for sintering, %									
FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	S	FeS ₂	C	volatiles	MnO
3,71	6,08	2,31	1,18	0,46	1,79	1,16	78,62	4,20	0,49
Chemical composition of manganese concentrate, %									
MnO	CO ₂	FeS ₂	Fe ₂ O ₃	P ₂ O ₅	SiO ₂				
44,56	19,33	2,25	1,79	0,31	12,40				
MgO	CaO	Al ₂ O ₃	K ₂ O+Na ₂ O	H ₂ O _n and others	loss at burning				
2.00	3.90	2.10	1.15	1.20	8.97				

Technological implementation

The manganese concentrate and coke breeze are with size which is over 30 mm. The vanadium catalyst is with size which is over 7 mm and they are not suitable for direct

agglomeration. It is necessary to accomplish of preliminary preparation of this materials – grinding and rolling. The grinding is going on in mechanical cylinder with working frequency of rotation – 25 rev/min. The continuance of grinding is 15 min to fraction (- 3 mm). The fraction (+ 3 mm) is going for new grinding [6-9]. The grinding materials there are following filling weights: Mn concentrate – 1,2 kg/dm³, V catalyst – 0,56 kg/dm³, coke breeze - 0,95 kg/dm³.

The rolling is accomplish in disk rolling machine with working frequency of rotation – 20 rev/min and slope of the disk – 45 °. The duration of rolling is 4 – 5 min. From the raw materials, in rolling machine was add 30 % return sinter from previous agglomeration. The dampness in the raw materials is about 4 % (0,25 kg for one portion raw materials). For the best rolling is add about 0,30 – 0,35 kg water for one portion raw materials and on this way is reach dampness of the raw materials about 9 %, which is normal for the sinter practice. At the bottom of the sinter cup (Figure 1, p. 7) is the grid and over it there is 2 – 3 cm return sinter (about 0,50 kg), from previous sinter process, but it is more coarse from the raw materials. The rolling is accomplish with the aim the sinter engine making better contact with the fractions of the concentrate and the catalyst and for more effective permeability of the gases to the raw materials from sinter process [6–9].

The sinter cup is with working volume 7,21 dm³. The data of the calculation program for raw materials are calculate from the volume of the sinter cup in the necessary kilograms for the three variants of sintering. First it is defy the volume of each raw material, which it fills in the working volume of the sinter cup, as take into account his filling weight. From the receiving volume with the help of filling weight is calculate the necessary weight of the respective raw component [1,10]. Because of the big heat loss from working with this size of the sinter cup in comparatively with sinter process from laboratory conditions, the volume of coke breeze is doubling [1].

At the first variant (80 % concentrate и 20 % catalyst), according to calculates of the program, are necessary 7,32 kg coke breeze and 135,68 kg mixture (concentrate and catalyst) for receiving to 100 kg sinter. The calculated data for the laboratory sinter cup for concentrate, catalyst and coke breeze are – 5,04 kg, 1,26 kg and 0,68 kg. The mixture for agglomeration at this variant is with weight 6,98 kg, as return sinter is 1,89 kg from this weight. The general weight of the mixture reply to volume about 7,19 dm³, which is approximately equal to the volume of the sinter cup.

At the double variant (70 % concentrate и 30 % catalyst), according to calculates of the program, are necessary 6,82 kg coke breeze and 132,89 kg mixture (concentrate and catalyst) for receiving of 100 kg sinter. The calculated data for laboratory sinter cup for concentrate, catalyst and coke breeze are – 4,11 kg, 1,77 kg and 0,61 kg. The mixture for agglomeration at this variant is with weight 6,49 kg, as return sinter is 1,76 kg from this weight. The general weight of the mixture reply to volume about 7,22 dm³, which inessential exceed the volume of the sinter cup.

At the three variant (60 % concentrate и 40 % catalyst), according to calculates of the program, are necessary 6,34 kg coke breeze and 130,21 kg mixture (concentrate and catalyst) for receiving of 100 kg sinter. The calculated data for laboratory sinter cup for concentrate, catalyst and coke breeze are – 3,30 kg, 2,19 kg and 0,52 kg. The mixture for agglomeration at

this variant is with weight 6,01 kg, as return sinter is 1,65 kg from this weight. The general weight of the mixture reply to volume about $7,21 \text{ dm}^3$, which is equal to the volume of the sinter cup.

The filling of raw materials is accomplished carefully to the walls of the sinter cup with the aim to avoid the congestion of the layer to the raw materials. The layer of the raw materials must to have optimal permeability of the gases. After the including of the vacuum installation is making a fire of upper layer to the raw materials with torch of gas. The time of the sinter process is about 25 min. Each minute is reading results for the temperature with thermocouple to voltmeter (Figure 1, p. 10) and the vacuum – with manometer (Figure 1, p. 9) [6].

RESULTS AND DISCUSSION

From the select three variants three sinters with 20, 30, and 40 % catalyst are received. Figure 2 show the parts of agglomerate with 70 % manganese concentrate and 30 % catalyst.



Figure 2 Sinter with 70 % concentrate and 30 % catalyst

The data from the measures of the temperature and the vacuum for these three processes of agglomeration are show in Figures 3 and 4.

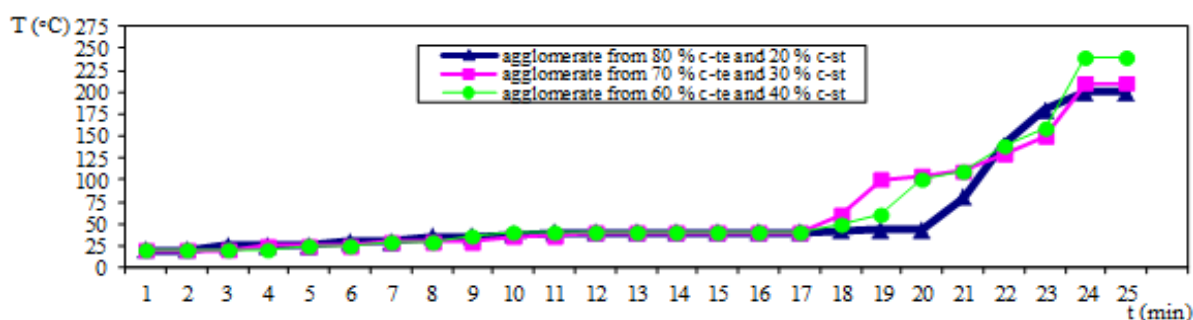


Figure 3 Changing of the temperature for the three sinter process

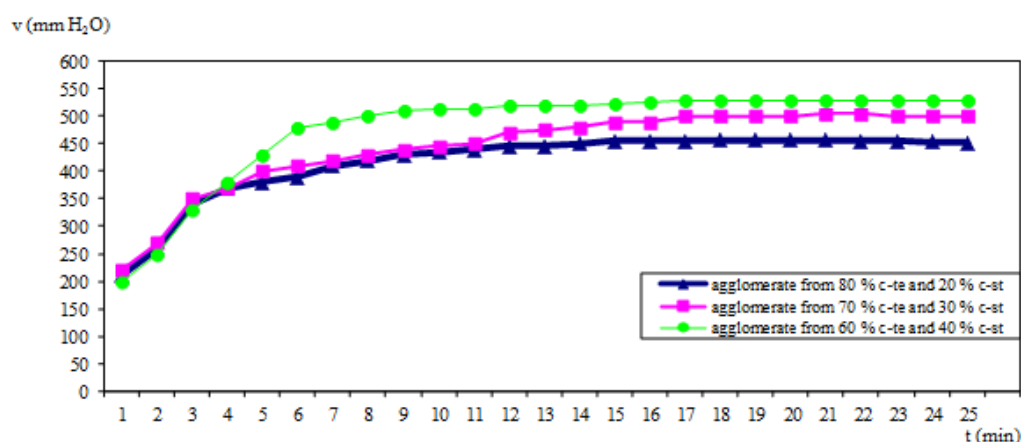


Figure 4 Changing of the vacuum for the three sinter process

According to the Figures 3 and 4 each of these three processes are with continuation about 25 minutes. The temperature of the process and necessary vacuum make increase with increase of quantity to the catalyst, because of more odds and ends, which is locate in the porous of the formation sinter. This follow to their occlusion especially in the variant with 40 % vanadium catalyst.

According to calculations making from a microscope drill the sinters there are following chemical composition, which is show in Table 2.

Table 2 Chemical composition of receiving sinters

oxide	sinter with 80 % c-te : 20 % c-st	sinter with 70 % c-te : 30 % c-st	sinter with 60 % c-te : 40 % c-st
MgO, %	6,11	5,80	5,40
FeO, %	3,77	3,68	3,59
SiO ₂ , %	18,30	23,61	18,51
Al ₂ O ₃ , %	4,87	4,64	4,41
MnO, %	60,59	53,67	47,03
CaO, %	6,09	5,48	4,89
V ₂ O ₅ , %	1,94	2,46	2,97

This chemical composition as independently definition can not explain chemical and structure characteristics of receiving sinters. For more entire picture of their complicated composition and fragmentariness has been making analysis with X-ray phases apparatus – TYR – M 62, with CoK_α ray and length of the wool of X-ray - $\lambda = 0,178892$ nm and computer record of receiving results. The data of analysis, accomplished with X-ray phases apparatus are show in Table 3.

In the diffraction picture of sinter with 100 % Mn concentrate are registered three basic crystal phases: MnO (manganosite), Mn₃O₄ (hausmanite) and 2MnO.SiO₂. At Table 3 we can see that from complex agglomeration of Mn concentrate with V catalyst, the lines of clean manganese oxides are displaced in direction to form of the alloys with SiO₂. This is due to the higher content of SiO₂ in waste vanadium catalyst (Table 1) and specifically conditions to the sinter process ($T \approx 1200$ °C).

Table 3 Composition of phases to the receiving sinters

sinter variant	80 % c-te : 20 % c-st	70 % c-te : 30 % c-st	60 % c-te : 40 % c-st
	2MnO.SiO ₂	Mn ₂ .SiO ₄	Mn.Mn ₅ .SiO ₂
fixed	SiO ₂ (α quartz)	MnO	V ₂ O ₄
crystal	SiO ₂ (α cristobalite)	V ₃ O ₅	V ₃ O ₅
phases	-	V ₃ O ₇	SiO ₂ (α cristobalite)
	-	SiO ₂ (α cristobalite)	-

The analysis accomplished with X-ray phases apparatus show availability of V₃O₅, V₃O₇ and V₂O₄ and the quantity of vanadium versus oxygen increase with the increase to percentage of catalyst in the sinter. The phases composition of sinter with higher contents of vanadium catalyst (30 and 40 %) is optimum for the aim of the next receiving to complex alloy.

From this analysis were not discovered phases of Fe and Ca.

The three sinters are with normal porous and structure. Their division of fraction is show in Table 4.

Table 4 Fraction composition of receiving sinters

80 % c-te : 20 % c-st			70 % c-te : 30 % c-st			60 % c-te : 40 % c-st		
fr. (mm)	kg	%	fr. (mm)	kg	%	fr. (mm)	kg	%
+30	3,400	61,10	+30	3,700	75,82	+30	3,100	61,37
+20	0,165	2,95	+20	0,100	2,05	+20	0,060	1,19
+15	0,055	0,99	+15	0,060	1,23	+15	0,000	0,00
+12	0,245	4,40	+12	0,220	4,51	+12	0,150	2,97
+5	0,580	10,42	+5	0,300	6,15	+5	0,560	11,09
-5	1,120	20,13	-5	0,500	10,25	-5	1,180	23,37
generally	5,565	100,00	generally	4,880	100,00	generally	5,050	100,00
loss	1,435		loss	1,620		loss	0,950	

The bases technological parameters of receiving sinters are show in Table 5. These are: production of sinter – A; sintering rate – V; quantity of good sinter – K; density – ρ; macro porous – δ; hardness – σ.

Table 5 Technological parameters of the sinters

technolog. parameters	80 % c-te : 20 % c-st	70 % c-te : 30 % c-st	60 % c-te : 40 % c-st
A, %	71,07	66,58	74,16
V, m/min	0,012	0,012	0,011
K, %	69,45	83,61	65,55
ρ, g/sm ³	3,38	2,76	2,52
δ, %	33	40	43
σ, kgp/sm ³	28	13	8

At the calculated parameters follow that with 30 % catalyst the production of sinter is least, but the percentage of good sinter is most. Sintering rate is comparatively constant and if we use 40 % vanadium catalyst we can see a little decrease. Density and compressive decrease with the increase of quantity to catalyst in sinter, because of the catalyst is brittle material. At the same time the macro porous increase because the vanadium catalyst there is a high

temperature of melting and its fragments don't suffer partial melting, like the fragments of manganese concentrate. This predispose, around each catalyst fragment to stick from partial melting concentrate and on this way the porous in the sinter will be increase.

Of the sinters considered, the variant with 70% manganese concentrate and 30% vanadium catalyst is most suitable (because $K = 83,61\%$) for subsequent high-temperature processing to an alloy containing vanadium. In this variant, a relatively high percentage of catalyst would be utilized.

CONCLUSION

It is elaborate a method for receiving of sinter from carbonate manganese concentrate and waste vanadium catalyst. For the first time is accomplish joint agglomeration of carbonate manganese concentrate and waste vanadium oxygen catalyst in laboratory sinter cup with correlation 80/20, 70/30 and 60/40.

Production of sinter, sintering rate and quantity of good sinter are normal. The hardness decrease with increase the quantity of catalyst. The sinters of this agglomeration processes there are a good porously and they are right for the next heat metallurgical manufacturing with carbon to complex alloy. The most suitable for this is the 70/30 sinter.

So far, the presented possibility for the utilization of a polluting product from the production of sulfuric acid is at the laboratory level. For processing the resulting sinter to an alloy with vanadium (which would find application in steelmaking as a deoxidizing and alloying alloy), it is necessary to carry out large-scale production of this sinter.

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