

THE TECHNOLOGICAL ASPECTS OF REDUCING THE EMISSION OF SULFUR DIOXIDE IN THE PROCESS OF SINTERING THE IRON ORE

UDC 632.15

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Abstract. *In this study are given the results of the researches about the gaseous sulfur compounds emission, converted to sulfur dioxide in the sintering process of the iron ore; in the ferrous metals Concern SARTID in Smederevo; as well as, the influence of the most important technological parameters of the sintering process on that emission.*

Key words: *emission of sulfur dioxide, sintering, iron ore*

1. INTRODUCTION

The tendency of contemporary ferrous metals in the world towards the development of the steel production, causes the increasing need for the mineral raw materials, wherefrom the steel is got. Concerning the fact, that today, there are a few ores which satisfy metallurgical demands, concerning the content of basic and accompanied metals, clearness granulometric structure etc; there is a need for their additional treatment for the quality improvement, economic value and ecological importance. Today, the sintering process is the most important way used for the improvement the raw materials quality that are processed in a blast furnace. The sintering process of iron ore is followed by a great emission of gaseous sulfur compounds into the atmosphere which takes to the human environment pollution.

According to certain evaluations, from the total emission of gaseous sulfur compounds in one forge, the emission in the sintering process of the iron ore is from 40% to 60%. However, from the total sulfur quantity, taken in by the mixture of raw materials for sintering; up to 95% is transformed, primarily in the form of their oxides: sulfur dioxide (SO₂), which makes about 70% of totally transformed sulfur and sulfur trioxide (SO₃); the share of which in the total emission is up to 30% [2].

In this study are given the results of the researches about the gaseous sulfur compounds emission, converted to sulfur dioxide in the sintering process of the iron ore;

in the ferrous metals Concern SARTID in Smederevo; as well as, the influence of the most important technological parameters of the sintering process on that emission.

The research is undertaken on the basis of production parameters realised in PI – Agglomeration Concern of ferrous metals SARTID – and literature [3,4,5]. In this research, the starting point is the functional technological thermodynamic dependance among the parameters of the sintering process of iron; on one side; and quantitative-qualitative indicators of the emission of sulfur compounds, created in the mentioned process, on the other side.

Using production-technological and literature data the emission of gaseous sulfur compounds is calculated; which are produced during sintering of the mixture of the known structure, chemical structure and the quantity, spent for one tone of sinter of the known chemical structures, in the period from 1984 – 1999.

By the analysis of the appearing conditions and estimation of the quantity of the gaseous sulfur compounds emission in the mentioned process, we wanted to establish:

- whether and to what extend it comes to exceeding the limit values of the emission (LVE) SO_2 from the pollution sources of agglomeration ferrous metals Concern SARTID.
- which are the most influential parameters of the sintering process on the creation of SO_2 .
- whether by the correction of technological parameters we can influence the reducing the emission of SO_2 from the sintering process.

2. RESULTS AND DISCUSSION

It may be considered that in the process of sintering the iron ore, the sulfur is transformed mostly in the form of its oxides SO_2 and SO_3 [6]. The emission of sulfur oxides, calculated on SO_2 , from all the sources of emission of sintering process of iron ore in SARTID, Smederevo enterprise part Agglomeration is shown on fig. 1.

The total mass emission of SO_2 , in the considered period, approximately was between 349-1883 mg/m^3 of smoke gases. The analysis shows that for the concerned period, there is the trend of great reducing of the emission SO_2 from these sources. In the 1980-s, of the analysed period; maximal values of the concentrations of emission of SO_2 were 1900 mg/m^3 of smoke gases, what is nearly $3 \times$ above the limit values of emission (500 mg/m^3). From 1992, the concentrations of the emission of SO_2 were constantly reduced and from 1996, under 500 mg/m^3 of smoke gasses, or that is to say under LVE. So the emission of sulfur dioxide, calculated on SO_2 , which in period from 1984-1990 was approximately 1730 mg/m^3 of smoke gasses, is reduced in the period from 1998-1999 averagely to 350 mg/m^3 of smoke gasses, that is to say about 5 times.

The sudden fall in the emission of SO_2 in the atmosphere begins in 1991 and 1992, when from 1880 mg/m^3 of smoke gasses, which was in 1990; it reduced to 1090 mg/m^3 in 1991, that is to say 540 mg/m^3 of smoke gasses in 1992.

The same trend of reducing, shows the factor of emission SO_2 as well; expressed in relation to the quantity of sinter or iron, taken from that sinter, fig 1b. In the period from 1984-1990, the average value of the emission factors SO_2 was 7,0 kg/t of sinter, while in period of 1996-1999 it was approximately reduced to 1,3 kg/t sinter, or about 5,3 times.

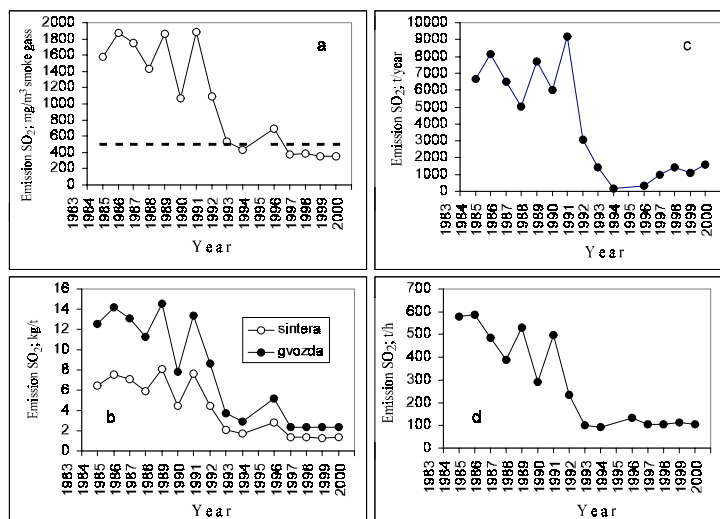


Fig 1. Movement of the average emission SO₂ by the years of concerned period from the process of sintering the iron ore in SARTID, Smederevo enterprise part Agglomeration (a broken line shows LVE)

Even bigger fall shows the factor of emission of SO₂ expressed in relation to 1 tone of iron, produced from sinter. From approximately 13 kg/t of iron in the period of 1984-1990, the factor of emission SO₂, has approximately fallen to 2,3 kg/t of iron, in the period 1996-1999, that is to say, something more than 5,5 times.

Concentration of SO₂, emitted in the atmosphere in this period is showed on the fig. 1c. Low values of concentration of the emitted SO₂ are registered during 1993 and after 1996. The consequences are of the range of the sinter production, as well as other factors. If the range of sinter production in 1984 and 1985 is compared to 1997, when approximately the same level of production is realised; it can be concluded that the concentration SO₂ emitted during the year in the atmosphere, is different for something more than 6000 t, or during 1997, in the atmosphere is emitted about 5,3 times less of SO₂.

In every hour of effective work of the sintering machine, it is emitted into the atmosphere, in the period from 1984-1991, approximately about 480 kg of SO₂ in the period from 1992-1999, averagely about 107 kg (fig. 1d).

So, the results about the emission SO₂ with the smoke gasses, made in the process of sintering iron row materials in SARTID, Smederevo enterprise part Agglomeration, shows that, starting from 1992-1999 it reduced a great deal. It is posed a question what influenced on the reduction of the emission of SO₂, or which are the factors that influence on appearance and selection of oxide sulfur in the process of sintering the iron ore. First of all, it should be mentioned the quantity of sulfur taken with the mixture for sintering (fig. 2.). On fig. 2, you can see remarkable direct corellation between the quantity of sulfur taken by the mixture for sintering and the dimension of the emission of SO₂, that is to say, by the increasing the quality of taken sulfur; increases the emission of SO₂ and v.v.

The quantity of totally taken sulfur into the sintering process, was about 4,0 kg/t of sinter, in the first part of the considered period, up to about 1,0 kg/t of sinter, in the period from 1996-1999.

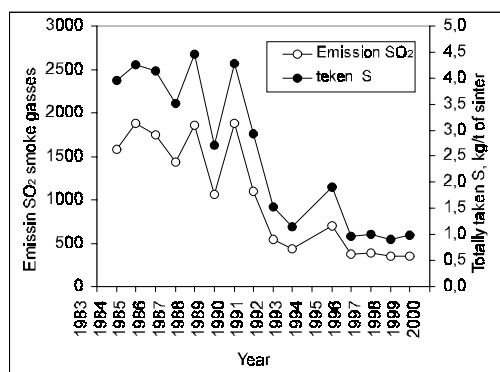


Fig 2. Dependence of the emission SO₂ from the quantity S taken with sintering mixture

The biggest amount of sulfur is taken into the sintering mixture with the raw material ore and coke [7,8]. The total quantity of taken sulfur by the iron ores, in the sintering mixture, in Agglomeration SARTID, Smederevo, in the period from 1984-1991, was approximately 43%. Coke, in the same periods approximately was 20% or 45% of sulfur. The smelters and the secondary raw materials take in small quantities of sulfur (under 10% from the totally taken quantity) [9,10].

Considering the fact, that the greatest part of sulfur is taken by the ore raw materials, so is their influence on the emission SO₂ remarkable, what can be seen on fig. 3.; where is given the dependance of the size of emission SO₂ from the quantity of the sulfur taken by the raw-materials and solid fuel. The influence of the quantity of sulfur taken by the solid fuel is less remarkable, although generally speaking, with the reducing the sulfur quantity, taken by the solid fuel, the emission of SO₂ is reduced as well.

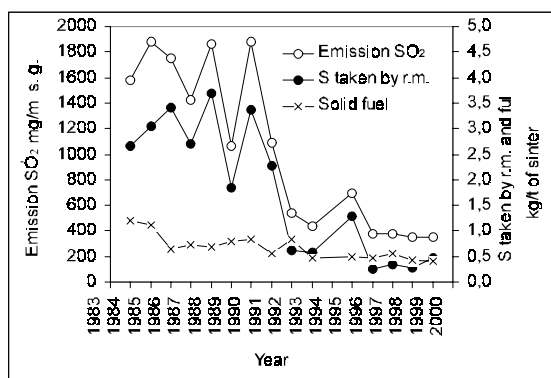


Fig. 3. Dependence the emission SO₂ from quantity S taken in by raw material and fuel

So, the content of sulfur in the raw materials has the remarkable influence on the emission SO_2 size, and that's why, you should use ores and concentrates with less possible content of sulfur. On the fig. 3., you can see that the content of sulfur in the ore mixture, used in the process of sinter production on Anglomeration SARTID in the period 1984-1999, was reduced from 0,30% what approximately was in period from 1984-1991, to approximately 0,05%, which was in period 1996-1999. The sulfur content in raw materials was reduced in the considered period 6 times. By the reduction, the quantity of sulfur taken by the mixture for sintering, didn't have the positive effects only on the emission SO_2 into the atmosphere, but also to the quantity of sulfur remained in sinter after the finished process of sintering (fig. 4). As you can see from the picture given, the content of sulfur in sinter is lower if by the sintering mixture is taken the lower quantity of sulfur.

However, you can't talk about the quality of ores and raw materials for iron production only from the aspect of the content of sulfur in them. The content of iron in the ore is, as well, very big parametre for evaluation their quality; not only considering the emission of gaseous sulfur compounds, but the other damaging gaseous compounds (nitrogen oxide and carbonic).

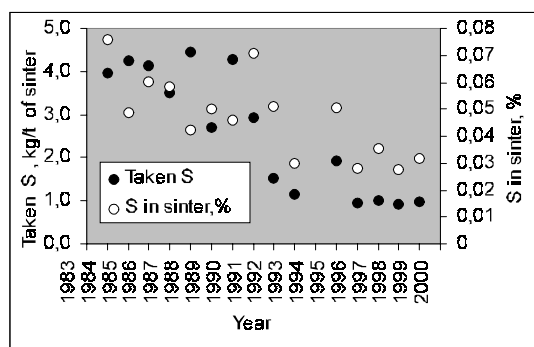


Fig. 4. Dependence of the content S in sinter from the quantity S taken in by the sintering mixture

The next parametre which influences the size of emission SO_2 is the degree of removed sulfur in sintering process. This influence is showed on the fig. 5. In the period 1984-1992, there is a clear correlation between these two sizes, well after 1992, that correlation is lost. As well, it can be seen that the degree of estranging sulfur from the sintering mixture before 1992 is approximately about 84%, and after, it is about 70%.

If the diagrams on the fig. 2, 5 are compared, you can see that the value of the transformation degree of sulfur and its influence on the size of the emission of SO_2 in correlation with the quantity of sulfur taken by the sintering mixture. So, till 1991, when, with the sintering mixture was taken in a big quantity of sulfur, the degree of its transformation was remarkably bigger, which had the effect on the size of emission of SO_2 . On the other side, in the period after 1991, in small amounts of sulfur in sintering mixture, the degree of removal of sulfur falls, and its influence on the size of emission of SO_2 is less shown.

In the sintering process, in the burning zone and in the zone of preheating the sintering mixture, they may absorb certain quantities of sulfur from the gaseous phase. It is the result of binding the sulfur compound from the gaseous phase with the appearing silicate solution of iron in the burning zone, in the form of the compound CaS . Besides, lime, limestone and calcium ferrites absorb SO_2 from smoke gases with the creation of calcium sulfate, which then on the temperature above 1000°C transforms into calcium sulfide.

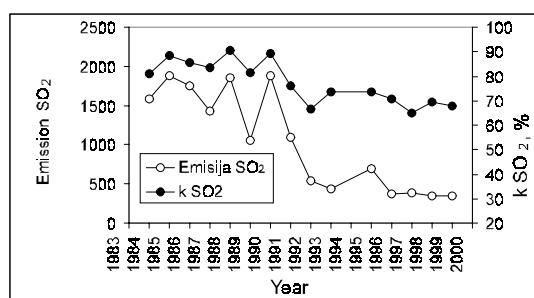


Fig. 5. The degree of estranging S in process of iron ore ($k \text{ SO}_2$) and its influence on the quantity of emission SO_2

In the moment when the threshold of the satiable mixture for sintering with sulfur, it comes to separation of sulfur with smoke gases. Well, with the same conditions of sintering, regardless to the quantity of sulfur taken in by sintering mixture, in the sinter should be absorbed the same quantity of sulfur. In other words, the degree of separation of sulfur will be lower at the mixtures for sintering that is lack with sulfur and v. v.

Besides the quantity of taken sulfur, to the degree of resulfuring the sintering mixture influences its structure as well; that is to say whether the taken sulfur is organic sulfide or sulfate origin. Sulfate sulfur is harder to remove from the sintering mixture because the thermic dissociation of sulfate starts yet at 1000°C and it speeds up with the higher temperature and by creating a liquid phase. That's why, the maximum degree of removing the sulfate sulfur during the sintering oxide ores, can be reached at relatively high expansion of the solid fuel, which is close to optimal, regarding from the point of view of solidness of sinter, and production range, fig. 6.

Further increasing of solid fuel consumption makes the degree of removal sulfate sulfur lower, because of the sulfate reduction reaction and the solution of the got sulfides in the iron solution.

The degree of sulfide sulfur, as well, in great measure depends on the consumption of solid fuel. However, as the difference from sulfate sulfur, by increasing the solid fuel consumption, the degree of estranging of sulfide sulfur ceases because of the increasing in the mixture for sintering, of the number of microvolume with very low partial oxygen pressure, as well as, because of increasing silicate solution of iron, which can dissolve a big quantity of FeS , especially in the presence of three-valence iron in the solution. From the solution, the sulfur is very difficult to remove by burning, because the reaction surface FeS in this fluid is very low, compared to fluid and solid FeS in raw mixture. The sulfur burning speed in this fluid phase depends on the oxygen diffusion in it, and is many times less than the speed of the chemical reaction itself.

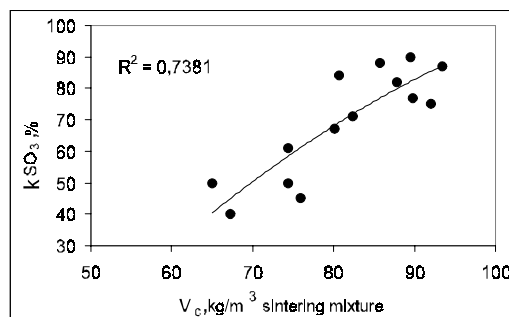


Fig. 6. The dependance of the sulfate removal degree ($k\text{SO}_3$) from the volume weight of s.f. in the sintering mixture (V_c)

For effective removal of sulfur from sintering mixture, it is necessary the oxidation atmosphere, and it is possible only with a small consumption of solid fuel. The influence of solid fuel consumption on the degree of sulfur removal is given on fig. 7.

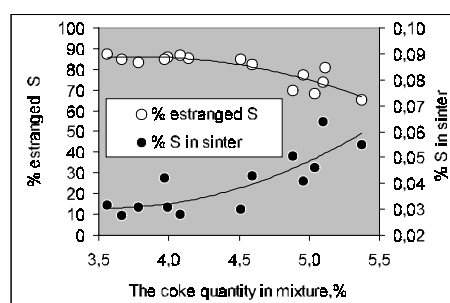


Fig. 7. The dependance of the degree of estranging S remained in sinter from solid fuel consumption

The next precondition for well resultfuring the sintering mixture is that it doesn't contain free lime (CaO). The lime as a strong base, makes a stable compound CaS , which stays in sinter. The influence of free CaO , or the increasment the baseness to the resultfuring degree of sintering mixture is showed on the fig. 8.

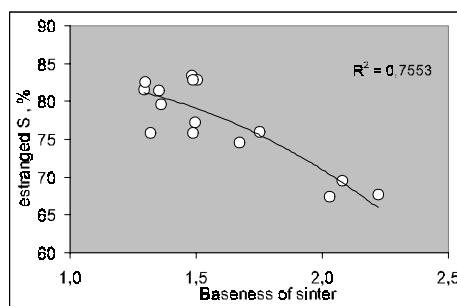


Fig. 8. The dependance of the degree of estranging S from baseness of sinter

At the end the size of ore particles is of decisive role for well resulfurring in the sintering process. Since the resulfurring process depends on burning, sulfur speed, which is the function of the size of it is reaction area, the speed of burning sulfur which is inside the ore particle depends on the speed with which the oxygen gets into the ore particle and on the speed with which SO_2 leaves the grain.

3. CONCLUSION

On the basis of analysis done, you can get the following conclusions:

- In the proces of sinter production on Agglomeration SARTID from the whole analyzed period 1983-1999, the emission of SO_2 was under LVE in the period 1996-1999.
- To the quantity of emitted SO_2 in the sintering of iron ore process, the greatest influence has the quantity of sulfur taken in by the sintering mixture, that is to say by ore and fuel.
- Concerning the fact that it is technically impossible, in the process of sintering to estrange the total quantity of taken sulfur, it is necessary to, in the case of exceeding the SO_2 emission into the atmosphere, reduce the sulfur quantity in the sintering mixture by providing ecologically high-quality ores for processing and to build in additional equipment for singling out SO_2 from smoke gasses.

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TEHNOLOŠKI ASPEKTI SMANJENJA EMISIJE SUMPOR DIOKSIDA U PROCESU SINTEROVANJA RUDA GVOŽDA

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U ovom radu dati su rezultati istraživanja emisije gasovitih jedinjenja sumpora, preračunatih na sumpor dioksid, u procesu sinterovanja ruda gvožđa u Koncernu crne metalurgije SARTID a. d. u Smederevu, kao i uticaj najvažnijih tehnoloških parametara procesa sinterovanja na tu emisiju.