LOGISTIC AND TECHNOLOGICAL ASPECTS OF APPLICATION OF TITANIUM-VANADIUM-MAGNETITE ORES IN SUWALKI BASIN IN POLISH METALLURGY

Ryszard BUDZIK, Lilianna WOJTYNEK, Ewa KULIŃSKA

University of Technology in Opole, Opole, Poland, EU,
r.budzik@po.opole.pl, *l.wojtynek@po.opole.pl*, *e.kulinska@po.opole.pl*

Abstract

In Poland titanium-vanadium-magnetite ore deposits are located near Suwałki. In the eighties and nineties of the last century, several research centers conducted research into the possible future use of these ores in the Polish metallurgy. The main purpose of these studies was to develop recovery methods for the vanadium and iron ores. The research was carried out in laboratory conditions, which was conditioned by a small quantity of several tons of these ores supplied from the future mine's wells. Research on the use of similar ores in Polish metallurgy was also carried out. Both laboratory and industrial research have enabled the development of a future technology for the use of Polish titanium-vanadium-magnetite ores in Polish metallurgy. Based on previous research, a hypothetical block diagram of vanadium logistics from Polish titanium vanadium magnetite ores can be created.

Keywords: Titanium-vanadium-magnetite ores

1. INTRODUCTION

The continuous development of the blast furnace process requires the use of a charge with appropriate physicochemical properties. The main components in blast furnace charge used in blast furnaces are mixtures of sinters and pellets with content more than 55% of iron.

Iron ore, mainly on the matrix mineral, hematite or magnetite mined in the form of a piece, as grain with too low iron content below 50%, are subject to appropriate enrichment and fragmentation. Grinded ores with grain size less than 1.0 mm called concentrates are subject to further processing in the sintering or pelletising process and the obtained product of appropriate quality in the form of sinter or pellets is the basic raw material for the production of pig iron in the blast furnace process. Nowadays in the sinter production are increasingly present in up to 100% of the stock concentrates of iron ores, mainly magnetite ores [1,4]. In Poland, iron metallurgy is fully based on imported iron ores.

Poland has rich deposits of magnetite ores containing also titanium and vanadium. In 1980-2000, in Poland, several research centers carried out research on the possibility of future use of these ores in metallurgy, mainly for vanadium and iron recovery. The main purpose of these studies was to develop recovery methods for these vanadium and iron ores.

2. THE ORE DEPOSITS OF TITANIUM - VANADIUM - MAGNESITE IN POLAND

Poland has rich deposits of complex ores, ilmenitic - magnetite containing also compounds of titanium and vanadium. In Poland, titanium-vanadium-magnetite ore deposits are located in the north-eastern region of Poland, not far from the city of Suwałki. The resources and average content of useful components of this deposit are presented in **Table 1.**

These ores belong to the type of complex ores, are located at a depth of 600 to 2000 m. They are mainly lenticular deposits up to 3 km long and up to 500 m thick, lying relative to the ground plane at an angle of 45 ° C on average. From the point of view of origin, these deposits should be included in the Baltic basin deposits. Inventories of these ore are estimated at around 1 billion tons [7].

Table 1 Resources and average content of useful ingredients [1,4]

Types ore	Resources in million tons	Fe %	TiO_2 %	V_2O_5 %
balance ores	957.2	27.8	7.4	0.27
off-balance ores	365.3	17.1	5.3	0.17

The main phase of this ore is Fe_3O_4 magnetite, $FeTiO_3$ ilmenite and Fe_2TiO. Studies have confirmed the small presence of solid hematite-ilmenite solutions. Some presence of gersenite mineral (Fe, Mg) Al_2 O_3 was also found in some ilmenite seeds. Magnetite in these ores occurs in grains up to a few millimeters and is distributed unevenly [2,3].

Vanadium in this ore occurs in the form of an isomorphic admixture in magnetite and it is relatively uniformly distributed throughout the entire volume of this oxide. Sulphides in ore occur mainly in the form of pyrrhotite, to a small extent also in the form of chalcopyrite and pyrite. Research on the use of Polish iron-containing titanium and vanadium ores in Polish metallurgy was carried out in several research centers (IMŻ Gliwice, AGH Kraków, Częstochowa University of Technology). A particularly large range of studies regarding the sintering process of mixtures containing vanadium - titanium - magnetite concentrates was carried out at the Częstochowa University of Technology. This is related to the strategic meaning of vanadium contained in this ore [4-7].

The results of research on the use of Polish ores containing iron, titanium and vanadium have been presented in over a dozen unpublished works and a dozen or so articles published in both Polish and foreign scientific journals [4-7].

Full, detailed results of these studies are presented in the monograph of the author R. Budzik [7]. Such research led to the determination of the technology of the future use of Polish ores with the content of iron, titanium and vanadium in the Polish iron metallurgy.

3. ENRICHMENT OF POLISH COMPLEX ORE

Polish complex ores containing titanium, vanadium, due to the low content of iron in them can not be directly applied to metallurgical processes. Therefore, they must be subjected to magnetic seperation and flotation. In Poland, in the Institute of Metallurgy, in Gliwice, it was found that the basic mineral useful in this ore is magnetite, ilmenite, and vanadium elements, titanium, cobalt and copper [7].

At the Institute of Ferrous Metallurgy, based on in-depth studies, a scheme of mechanical processing of Polish complex ores was developed in the form of:

- initial crushing to grain size of 15 mm with magnetic seperation of lump ore, with separation of gangue destined for construction aggregate,
- crushing and wet grinding to a grain size of less than 0.25 mm,
- flotation of ore sulfides to obtain a sulphide product containing valuable alloying elements,
- seperation in a high magnetic field to obtain a magnetite concentrate [3].

It was found that as a result of applied magnetic separation, magnetite concentrate contains from 63 to 65% Fe, 3.3, to 3.4% TiO_2, 0.43 to 0.44% V, 1.0 to 2.0% SiO_2 and 0.1 to 0.3% S. Content above 0.40% V in the concentrate, allows the extraction of this element from vanadium - titanium - magnetite ore by using a pyro hydrometallurgical process or a purely metallurgical process. The pyro hydrometallurgical process of vanadium extraction is very disruptive due to environmental criteria. Vanadium extraction can also be carried out by producing vanadium, which is subjected to oxidation in an oxygen converter to obtain vanadium slag from which vanadium is isolated.

4. THE ORE DEPOSITS OF TITANIUM - VANADIUM - MAGNESITE IN POLAND

Currently, in the world the production of pig iron is based almost entirely on the stock consisting of sintered or clumped, formed from hematite ores and magnetite concentrates, in which titanium and vanadium is a small admixture, amounting to an average of hundredths of a percent. In two countries, in Russia and Finland, is used in a small extent for the production of pig iron, vanadium -titanium - magnetite concentrates, only due to the production of vanadium. Vanadium from Polish complex ores can be obtained in two ways [4]:

- through the so-called pyro-hydrometallurgical process,
- through a purely metallurgical process.

The first method presented by the IMŻ in Gliwice consists in:

- pelleting vanadium - titanium - magnetite concentrate containing vanadium with the corresponding addition of sodium salts, most commonly sodium carbonate Na_2CO_3,
- oxidation at the temperature of approx. 1350°C microtubes resulting from pelletization,
- leaching of oxidised microclusts in an ammonium sulphate solution $(NH_4)_2SO_4$ in temperature 80 do 90°C where polyvinyladian sodium $(NH_4)_2V_6O_{16}$ is formed, which, when properly heated, decomposes and forms vanadium oxide V_2O_5 from which pure vanadium is obtained [3].

The pyro-hydrometallurgical treatment allowed to recover about 83% of the vanadium contained in the concentrate. This way of obtaining vanadium has many opponents taking into account the protection of the natural environment. In the case of Polish conditions, it would be necessary to construct expensive facilities and equipment that would meet very high criteria for environmental protection.

The second method of vanadium production presented by the Częstochowa University of Technology consists in:

- obtaining pig-iron with content of vanadium,
- the use of such pig iron as the feed to the converter process,
- obtaining a converter slag containing vanadium in the form V_2O_5 and extraction of vanadium from slag [7].

It follows from the above considerations that the charge for the blast furnace process may be sintered with iron, titanium and vanadium.

5. RESEARCH AND PERSPECTIVE OBTAINING VANADIUM FROM POLISH COMPLEX ORES BY METALLURGIC METHOD

Vanadium from complex ores containing vanadium compounds is produced in only a few countries around the world [7]. The mineralogical specificity of such ore is so complicated that in each case, its own methods of obtaining this element are elaborated. From the point of view of the current technical and technological conditions, a more promising way of developing Polish complex ores to obtain vanadium will be their use in a purely metallurgical variant, where sintered iron, vanadium and titanium could be used as a basic charge in metallurgical processes to obtain vanadium-containing slag, and then by extraction from this vanadium slag. The use of such complex ore processing method in the future seems to be much more reasonable and acceptable. Comprehensive research on the use of Polish complex ores in metallurgy was carried out at the Częstochowa University of Technology [4-7].

The results obtained from these studies were presented in over a dozen reports on scientific papers and scientific articles in both Polish and foreign magazines. The main objective of the sintering process of blends with various concentrations of vanadium - titanum - magnetite concentrate and their various basicities was to determine the basic metallurgical properties such as: strength, breakability, reductionability and softening range. An important goal of this research was to investigate processes affecting the final phase and mineralogical composition of sinters, mainly in relation to vanadium and titanium minerals.

To this purpose, a comprehensive study was carried out, taking into account the full share of 0 to 100%, complex ore concentrates in ore mixtures in the field of CaO/SiO_2 from 0,1 to 4,0.

On average, Polish concentrates contain about 0.44% vanadium. With such vanadium content, its production is likely to be profitable in the future.

The results of laboratory tests regarding the use of concentrates from polish complex ores in the sintering process have been confirmed in the industrial sintering test [4,7], and the use of the sinter obtained in the industrial test of pig iron production.

In the industrial test was entered into the blast furnance charge alkaline iron titanium sinter in the amount of 200 kg / Mg pig iron [4]. Technological parameteres obtained in this test were not worse than the production parameters of a blast furnace working on a charge consisting of 100% of a self-melt sinter including concentrates of ores without increased amount of titanium and vanadium.

The research determined the effect of alkalinity, CaO/SiO_2 and the proportion of concentrate on some basic metallurgical properties of the sinter, such as: strength, breakability, yield, reductionability, softening range, chemical composition, mineralogical composition.

The scope of the research included sintering of mixtures containing various proportions (100%, 60% and 20%) of concentrates of complex ores in an ore mix of basicity CaO/SiO_2 equal to 0.1; 1.0; 2.0; 3.0 and 4.0.

The composition of sinter mixtures included, in addition to the vanadium- titanium- magnetite concentrate, also hematite ore, limestone and fly-ash.

Attempts to sinter mixtures with alkalinity of 0.1; 2.0; 3.0; 4.0; 8.0 and 100%, 60% and 20% concentrate allowed to determine the influence of these factors on the metallurgical properties of the sinter.

One of the most important criteria for assessing the suitability of sinters for the blast furnace process is the indicator of their strength and breakability.

The previous dozen-year study on determining the strength properties of sinters used in Poland, allowed to determine the minimum range of strength values. The minimum of this range is 65%, while for crumbling the maximum is 40%. Based on the test results, it should be noted that the average indexes of about 65% were characterized by sinters made from blends containing 60% and 20% concentrate in the entire range of CaO/SiO_2 basicity from 1.0 to 4.0. The data show that the reduction of fractions changes with increasing alkalinity, CaO/SiO_2. For sinters containing 60% and 20% concentrate, the highest reductivity of 69 to 75% was obtained for sinters with CaO/SiO_2 basicity from 1.0 to 3.0. One of the basic conditions for the efficiency of sinter strands is the use of mixtures with optimum breathability affecting sintering time and linear sintering speed. The data show that for each sintering series the speed increases with increasing CaO/SiO_2. The lowest sintering speeds of 17.9 to 20.3 mm / min were obtained by sintering mixtures without the addition of limestone, the highest being 32.7 to 34.1 mm / min with a basicity of CaO/SiO_2 equal to 4.0. The sintering time of the blends did not differ from those obtained under industrial conditions.

Tests in laboratory conditions, taking into account the criterion of sinter quality assessment, showed the possibility of introducing polymetallic polymer concentrates into sintering mixes up to 60%. An important result of this research was the presentation of the identification of the phase and mineralogical composition of the sinters obtained.

The research included qualitative and quantitative analysis of the distribution of Fe, Ti, Al, Mg, Ca, Si and V elements in selected micro-areas of the tested sinter.

The creation of phases with calcium predominantly containing titanium and mainly the formation of crystalline elemental grains is explained in a scientific manner.

The results of laboratory tests of the sintering process were verified in industrial conditions and presented in domestic and foreign magazines [4-7]. A 12-day industrial test carried out in industrial conditions confirmed the possibility of sinter production, and what is very important confirmed the possibility of introducing such sinters for the production of pig iron with an increased content of titanium.

The use of sinter containing complex ore for the production of pig iron in industrial conditions in the blast furnace process did not cause negative results, on the contrary, better production rates were obtained during the industrial test compared to the production of pig iron from the sinter feed containing no complex ore.

6. THE FUTURE LOGISTIC ASPECT OF THE USE OF POLISH COMPLEX ORES FOR VANADIUM PRODUCTION

In the future, Polish complex ores containing vanadium, titanium and iron may be developed using two pyro-metallurgical and pure metallurgical pathways. The adoption of one or the other method will entail the construction of many plants ranging from the construction of an ore mining mine to the final plant of vanadium extraction from the vanadium pentoxide extraction (V_2O_5).

The logistics aspect in the application of the pyro-hydrometallurgical method would be as follows:

- mine construction,
- construction of a magnetic separation plant to obtain a magnetite concentrate,
- construction of a concentrating pellet plant,
- construction of a leaching plant for oxidized microtubes,
- construction of vanadium extraction plant.

The simplified logistic aspect of vanadium production would be:

- mine construction,
- construction of a magnetic separation plant to obtain a magnetite concentrate,
- production of sinter containing concentrate in existing ironworks in Poland,
- production of pig iron containing vanadium in existing ironworks in Poland,
- vanadium production by extraction of V_2O_5 from slag.

Considering these two ways, it is more likely to use a vanadium method of pure metallurgy. In this case, it is only necessary to build a mine, a magnetite plant and a vanadium extraction plant from slag.

The first pyro-hydrometallurgical method should be rejected due to the construction of many plants, as well as due to environmental protection.

7. CONCLUSION

Research on the application of Polish complex ores containing vanadium and titanium in Polish metallurgy was carried out in several research centers in the country (IMŻ Gliwice, AGH Cracow, Częstochowa University of Technology). A particularly large range of research on the sintering process of mixtures containing concentrates of titanomagnetite was carried out at the Częstochowa University of Technology.

The results of research on the use of polish complex ores have been presented in over a dozen unpublished works and over a dozen articles published in both Polish and foreign scientific journals.

Such research led to the determination of technology for the use of Polish polymetallic ores in iron metallurgy.

Presentation of the results of both published and unpublished studies may limit in the future, and perhaps eliminate in the future, tedious and expensive research, which will be helpful before the decision to build Polish mines of Polish complex ores containing vanadium and titanium.

It seems that the subject of Suwałki ore, due to its uniqueness, he will soon return to the evaluation of practitioners and scientists.

REFERENCES

[1] BOŁD T., KUZIAK, R. Charakterystyka faz zawierających tytan w rudzie polimetalicznej*. Prace Instytutu Metalurgii Żelaza. Gliwice*. 1983, nr 3-4, pp.146-149.

[2] ZIELIŃSKI, S. Problemy flotacyjnego wzbogacania rudy tytanomagnetytowej. *Prace Instytutu Metalurgii Żelaza. Gliwice.* 1983, nr 3-4, pp.119-122.

[3] BOŁD, T., KUZIAK, R., PADUCH, J. Identyfikacja składników fazowych w koncentracie tytanomagnetytowym*. VI krajowe Sympozjum Mikroanalizy Rentgenowskiej Ciał Stałych*. Jabłonna.1986, pp.101-105.

[4] BUDZIK, R. Badania nad zastosowaniem polskich rud polimetalicznych w metalurgii*. Hutnik - Wiadomości Hutnicze*. 2008, nr 7, pp. 327-331.

[5] BUDZIK, R. Titan in the Process of Pig Iron Smelting. *Metallurgy Croatia*, 2002, no 1, pp. 241-243.

[6] BUDZIK, R. Behaviour of titanium compounds in the sintering process of titanium-magnetite ores. *Metallurgy Croatia*. 2005, no 3, pp.179-182.

[7] BUDZIK, R. Rudy magnetytowe i hematytowe w procesie spiekania. Częstochowa. *Monografia*. 2010, nr 4, pp.119-182.