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UTILIZATION OF THE STEELMAKING SLAG BY REDUCTION WITH THE USE OF THE MODIFIED THE CHEMICAL COMPOSITION OF THE INPUT MATERIAL

ZAGOSPODAROWANIE ŻUŻLI STALOWNICZYCH POPRZEZ ZASTOSOWANIE METODY REDUKCJI I MODYFIKACJI SKŁADU CHEMICZNEGO MATERIAŁU REDUKOWANEGO

Utilization of the steelmaking slag by reduction is the technology which seems to be today rather controversial. However it is possible to use this way of utilization in case if the economical surround will be changed. One of the possible improvement for the described method is the modifying input materials for process reduction. The thermodynamic model was developed which enable to optimize the chemical composition of the final product. The laboratory investigations confirmed a good agreement between model calculations and experimental results.

Keywords: slag, utilization, reduction, modeling

Zastosowanie technologii redukcji żużla do utylizacji żużli stalowniczych wydaje się być dzisiaj pomysłem kontrowersyjnym. Jednakże wybór tej ścieżki utylizacji może stać się prawdopodobny w sytuacji zmiany warunków ekonomicznych w otoczeniu branży hutniczej. Jedną z metod udoskonalenia rozważanej technologii jest zastosowanie metody modyfikowania materiału wejściowego do procesu redukcji. Opracowany został model termodynamiczny, który umożliwia optymalizację składu chemicznego finalnego produktu prowadzonego procesu. Badania laboratoryjne potwierdziły dobrą zgodność obliczeń modelowych z wynikami eksperymentów.

1. Introduction

The development of modern industrial processes must take into account not only factors related to the product quality assurance and its manufacturing cost but also noxiousness to the environment. The policies related to the creation of environmentally friendly processes already constitute a sustainable element of global economic development. The trends mentioned concern not only new processes but affect existing processes as well, forcing us to look from a new standpoint upon the existing practice of using natural resources.

The steel industry is a classic example of an industry which is subject to far-reaching transformations with regard to the improvement of standards concerning environmental pollution. A comparison of the present-day intensity of emissions of a typical integrated steelworks with the corresponding level a dozen or so years ago is the best example of the development of methods which reduce the noxiousness of steel plants. Efforts to develop waste-free processes are at present among the most frequently applied solutions.

Both the slags formed at the iron making stage in blast furnaces and the steelmaking slags from BOF and EAF processes hold a special place among the waste materials produced by the steel industry. Blast furnace slags do not pose a problem nowadays, and they are 100% processed into fully usable products such as blast-furnace cement or mineral wool. The steelmaking slag problem is entirely different. Due to their chemistry the steelmaking slags are noxious waste, and it is difficult to find an economical method of their utilization. Until recently these slags had been disposed of in slag dumps. Attempts to use steelmaking slags as a substitute for natural aggregates in road construction have been made for some time. Taking into account the intensity of the road infrastructure development, it seems a perfect solution to the problem. Unfortunately, the preparation of slag as a road construction material is not without its drawbacks. After completion of the steelmaking process, the slag

basicity measured as the ratio of percentages of CaO and SiO_2 ranges from 2 to 4.

It causes the formation of unstable eutectics in the slag during the solidification stage. Morphological changes occurring in the slag after its solidification take a long time and are related to a change in the volume. This all causes serious problems with the preparation of slag as an aggregate for road construction. The process of slag mineralogical constitution modification should be finished before it is used as a construction material otherwise the change in the slag aggregate volume will result in the cracking of the newly built road surface.

The steelmaking utilization characteristics presented above indicate the need for slag to be stored in slag dumps, either permanently or temporarily. The cost of dumping is an arbitrary decision and along with the change in the rate for storing this waste, the market conditions regarding attainable methods of utilization will also change.

Therefore, looking for other methods of steelmaking slag utilization is a very topical task. Subjecting the slag to the reduction process and obtaining a semi-product for cement, fertilizer or refining slag manufacturing can be among these methods. At the current storage rates implementation of such processes is not economically viable, however a change in storage costs may alter this situation.

2. The concept of modification of the slag composition at the liquid phase stage

When we assume that deliberations on steelmaking slag reduction are acceptable, the question of the practical execution of this process and the possibilities of obtaining the assumed chemical composition of the target material arises. The slag reduction process consumes a vast amount of energy and this fact has the biggest influence on the process viability. Therefore the main assumption of the process developed should be the use for the reduction of slag still in the liquid or semi-liquid state. It will allow the reduction of energy demanded by the value of the physical heat of the liquid slag. Subject to demand, the slag reduction process may yield the following materials:
- Material for blast furnace cement production
- Fertiliser
- Refining slag

Each of these materials is characterised by a different chemical composition and also the share of the reduced slag phase varies. However not all the above mentioned products can be manufactured from a slag of any initial composition. This fact becomes a serious hindrance, as it significantly raises the level of difficulties

of the reduction process control. The presence of heavy metals in slag practically excludes it from its use as a fertilizer. On the other hand too high a mass percentage of silica makes it difficult to create a composition which is acceptable as the refining slag composition. Even such a superficial problem analysis leads to the clear conclusion that, subject to the needs, the mass of the steelmaking slag reduced should be supplemented by additives ensuring that the desired target composition of the reduced material is obtained. However, it is known that the chemical composition of the steelmaking slag is unstable. In addition, composition modifiers, which should be bauxite and burned lime, are also characterized by some fluctuations of the content of their main components. Therefore a proper selection of the mass of materials modifying the slag reduced should be based upon the knowledge of masses and chemical compositions of all charge components and on the a priori assumed parameters of the output material chemical composition. The degree of complexity of a problem so defined is very high and gives rise to doubts about the possibilities of its execution.

The task solution concept presented is based upon the assumption that the process should be carried out in a manner enabling a state near the equilibrium to be obtained and the thermodynamic model to be used for calculations. The Department of Ferrous Metallurgy of the Faculty of Metals Engineering and Industrial Computer Science of AGH University of Science and Technology has the package for thermodynamic calculations FactSage[TM] and the environment for object-oriented process modelling with the use of the FACT library, the so called SimuSage[TM]. With the use of both mentioned tools an application enabling both the control of the steelmaking slag reduction process to be examined and the charge composition to be optimised has been created.

3. Laboratory tests of the BOF slag reduction process

Laboratory stand.
An induction furnace of the nominal capacity of 10 kg was used for the slag reduction process tests. The charge was melted in a graphite crucible. In order to check the effect of the crucible material on the slag the so-called "blind test" was carried out, by melting slag without any additives and watching the change in its chemical composition. As the experiment time was only 20 minutes the test showed a small effect of the crucible material on the slag chemical composition change. With the described test the optimum mass of the charge necessary for the experiments was also determined. It was

assumed that the completion of each experiment would be determined by the end of the foaming period of the reduced slag, although no sooner than 15 minutes.

Findings of laboratory tests

The objective of the conducted tests was to check the possibility of approaching the state of equilibrium during the reduction of BOF slag with the addition of graphite and variable additions of bauxite and lime. Tables 1 and 2 present information on masses and chemical composition in 7 conducted tests.

TABLE 1

Mass of the BOF slag and modifiers

No.	Mass of slag [g]	Bauxite [g]	Lime [g]
1	500	50	0
2	500	60	0
3	500	65	0
4	500	70	0
5	500	100	0
6	400	220	0
7	300	150	150

TABLE 2

The chemical composition of the BOF slag and the slag modified with the additions of bauxite and lime

No.	The chemical composition of the charge before the reduction										
	MnO	FeO	MgO	Al_2O_3	SiO_2	CaO	TiO_2	K_2O	Cr_2O_3	P_2O_5	S
0	2.36	20.75	4.56	0.84	17.76	47.79	0.18	0.80	1.60	1.07	0.050
1	2.14	19.00	4.14	8.75	16.69	43.47	0.51	0.72	1.45	0.97	0.045
2	2.11	18.69	4.07	10.17	16.50	42.70	0.57	0.71	1.43	0.96	0.04
3	2.09	18.54	4.04	10.86	16.41	42.33	0.60	0.71	1.42	0.95	0.04
4	2.07	18.39	4.00	11.54	16.32	41.96	0.63	0.70	1.40	0.94	0.04
5	1.96	17.54	3.80	15.35	15.80	39.87	0.79	0.66	1.33	0.89	0.041
6	1.52	13.91	2.94	31.76	13.58	30.93	1.48	0.51	1.03	0.69	0.032
7	1.18	10.75	2.35	22.41	10.75	47.47	1.05	0.40	0.80	0.53	0.025

0 – the base composition of BOF slag,
1 – BOF slag with 10% bauxite addition + 6% graphite (25 min)
2 – BOF slag with 12% bauxite addition + 5% graphite (21 min)
3 – BOF slag with 13% bauxite addition + 5.5% graphite (25 min)
4 – BOF slag with 14% bauxite addition + 6% graphite (21 min)
5 – BOF slag with 20% bauxite addition + 6% graphite (21 min)
6 – BOF slag with 55% bauxite addition (fulfilment of proportion $12CaO * 7Al_2O_3$) + 6% graphite (19 min)
7 – BOF slag with 50% bauxite addition + 50% lime addition + 6% graphite (19 min)

In each of the experiments conducted a reducer in the form of graphite was added and its given percentage was calculated relative to the mass of the slag used. Having finished reduction and cooling the samples down the non-metallic phase formed was analysed. The experiment findings are presented in the Table 3.

The results of the analyses were then compared with the theoretical state of equilibrium reached by the system at a temperature of 1650°C. The comparative analysis is to determine if the state of thermodynamic equilibrium is the right state of reference to make decisions on composing the charge for the reduction process. The results of the calculations of the states of equilibrium for all seven experiments are presented in Table 4.

TABLE 3

The chemical composition of the reduced phase obtained

No.	MnO	FeO	MgO	Al$_2$O$_3$	SiO$_2$	CaO	TiO$_2$	K$_2$O	Cr$_2$O$_3$	P$_2$O$_5$	S
1	1.08	1.41	4.89	11.36	21.66	56.41	0.65	0.31	0.55	0.04	0.06
2	1.44	1.08	5.16	13.07	21.20	54.86	0.73	0.33	0.44	0.53	0.06
3	0.89	0.79	5.06	14.00	21.13	54.61	0.77	0.25	0.32	0.23	0.06
4	1.33	1.08	4.81	14.78	20.86	53.85	0.77	0.33	0.57	0.16	0.05
5	1.62	1.31	4.58	19.28	19.71	50.11	0.93	0.36	0.61	0.34	0.05
6	1.49	1.82	3.43	37.43	15.52	36.47	1.65	0.31	0.384	0.01	0.04
7	1.04	1.50	2.62	25.58	12.27	54.19	1.18	0.20	0.30	0.01	0.03

TABLE 4

The equilibrium chemical composition of the non-metallic phase (FactSage^{TM})

No.	MnO	FeO	MgO	Al$_2$O$_3$	iO$_2$	CaO	TiO$_2$	K$_2$O	Cr$_2$O$_3$	P$_2$O$_5$	S
1	0.09	0.02	5.14	11.95	22.76	59.26	0.68	0.05	0.01	0.00	0.00
2	0.91	0.14	5.36	13.56	22.00	56.86	0.76	0.17	0.01	0	0
3	0.44	0.05	5.24	14.49	21.88	56.84	0.80	0.12	0.01	0.00	0.00
4	0.14	0.01	5.05	15.52	21.90	56.40	0.81	0.08	0.01	0.00	0.00
5	0.20	0.01	4.83	20.32	20.77	52.72	0.98	0.11	0.01	0.00	0.00
6	0.47	0.01	3.61	39.37	16.33	38.31	1.74	0.19	0.01	0.01	0.01
7	0.18	0.02	2.73	26.64	12.76	56.37	1.23	0.09	0.01	0.01	0.01

The findings presented in Table 4 indicate that in the state of equilibrium both the levels of ferrous oxide and manganese oxide contents are slightly higher than those determined by experiments. However, taking into account the initial content of ferrous oxides in the slag reduced, one should acknowledge that the process conducted significantly approaches the state of equilibrium. Hence the conclusion that the static model of the slag reduction process control may be based on a thermodynamic model. The experiments conducted showed the possibility of controlling the final composition of the resulting non-metallic phase in a rather wide range, meaning there are vast possibilities in the use of the method for production of the assumed semi-products.

The practical execution of the process described is however related mainly to the problem of variability of the chemical composition of components of the charge. Every single process requires an individual calculation of the excess charge, taking into account the chemical compositions of all materials in the charge. Therefore, it is necessary to develop an algorithm, which will enable this task to be performed in a flexible way depending on the type of the product to be produced.

4. The concept of the model for calculating the charge for the reduction process

A tool for the calculation of the chemical composition of the reduced phase should enable a few basic criteria to be met i.e. reaching the liquidus temperature, the ratio CaO/Al$_2$O$_3$ and the FeO content. The assumption was to create an optimization procedure, enabling the significance of individual criteria to be defined in a flexible way. The detailed description of the algorithm applied is as follows:

At the beginning of the optimisation procedure the user sets:

- the chemical composition and the mass of slag,
- the additives used for reduction,
- the demanded final process parameters, such as the liquidus temperature Tg, the ferrous oxide content in the slag Feg and the ratio CaO to Al$_2$O$_3$ ag.
- the weights of the optimisation procedure, so that the user can determine what significance during optimisation should be assigned for:
  - the liquidus temperature of the final phase approaching the arbitrary assumed value Tg,

- the final mass of ferrous oxides approaching the value Feg,
- the final value of the ratio CaO/Al$_2$O$_3$ approaching the value ag.

Next the initial masses of additions are determined by random.

For such a defined system (the composition and the mass of slag and additives) the liquidus temperature, or the temperature of the system in which no solid precipitations appear in the slag, is determined.

The system calculates the final mass of ferrous oxides and the ratio CaO/Al$_2$O$_3$ for a given temperature, and then the value of the objective function as the sum of differences between the demanded system parameters (Tg, Feg, ag and the corresponding actual values) multiplied by the weights of the optimisation procedure.

In subsequent steps the additive masses are altered ranging from 1 kg to 10% of the current additive mass and the liquidus temperature, and the final value of the CaO/Al$_2$O$_3$ ratio, the ferrous oxide content, and the objective function value are re-calculated. If the value of the new objective function is lower then the minimum of the objective function value found so far, the current additive masses are assumed as the base masses for the following steps of the optimisation procedure.

The steps including the change in the additive mass, the calculation of the new final system parameters and the determination of the new objective function are re-iterated until a lower value of the objective function is not found in the consecutive 20 steps.

Fig. 1 shows the algorithm of the program for optimisation of the input material mass for the assumed final parameters of the system.

The above application enables virtual experiments to be carried out, allowing the real process results to be foreseen. The tool is helpful both at the new process planning stage and in the future real process control.

5. Model simulation results

The objective of the model calculations was to check the influence of variability of the chemical composition of the non-metallic phase forming from the slag reduction on the temperature of the obtained phase and on the attainable CaO/Al$_2$O$_3$ ratio. The most interesting issue is the observation of changes in the properties of the product obtained at composition modification by enrichment of the input material by Al$_2$O$_3$. To this end a typical BOF slag composition was used, which was then modified so that only the basicity changed from 2.5 to 3.5. Altogether the calculations were carried out for five various slag basicities. In addition, for each set basicity varied additions of Al$_2$O$_3$ were simulated, ranging from 0 to 30% of the slag mass.

The findings are presented in Fig. 2. As expected, a very clear effect of the Al$_2$O$_3$ addition on the change in the liquidus temperature of the product can be observed. The effect of basicity is difficult to be evaluated on a 3D graph and therefore the graph shown in Fig. 3 was generated on the basis of the same result database. It follows that the effect of the slag basicity on the liquidus temperature declines with the increase of the Al$_2$O$_3$ content in the charge. At the same time it is noticeable that the threshold above which the basicity influences the liquidus temperature increases along with the increase in the Al$_2$O$_3$ share.
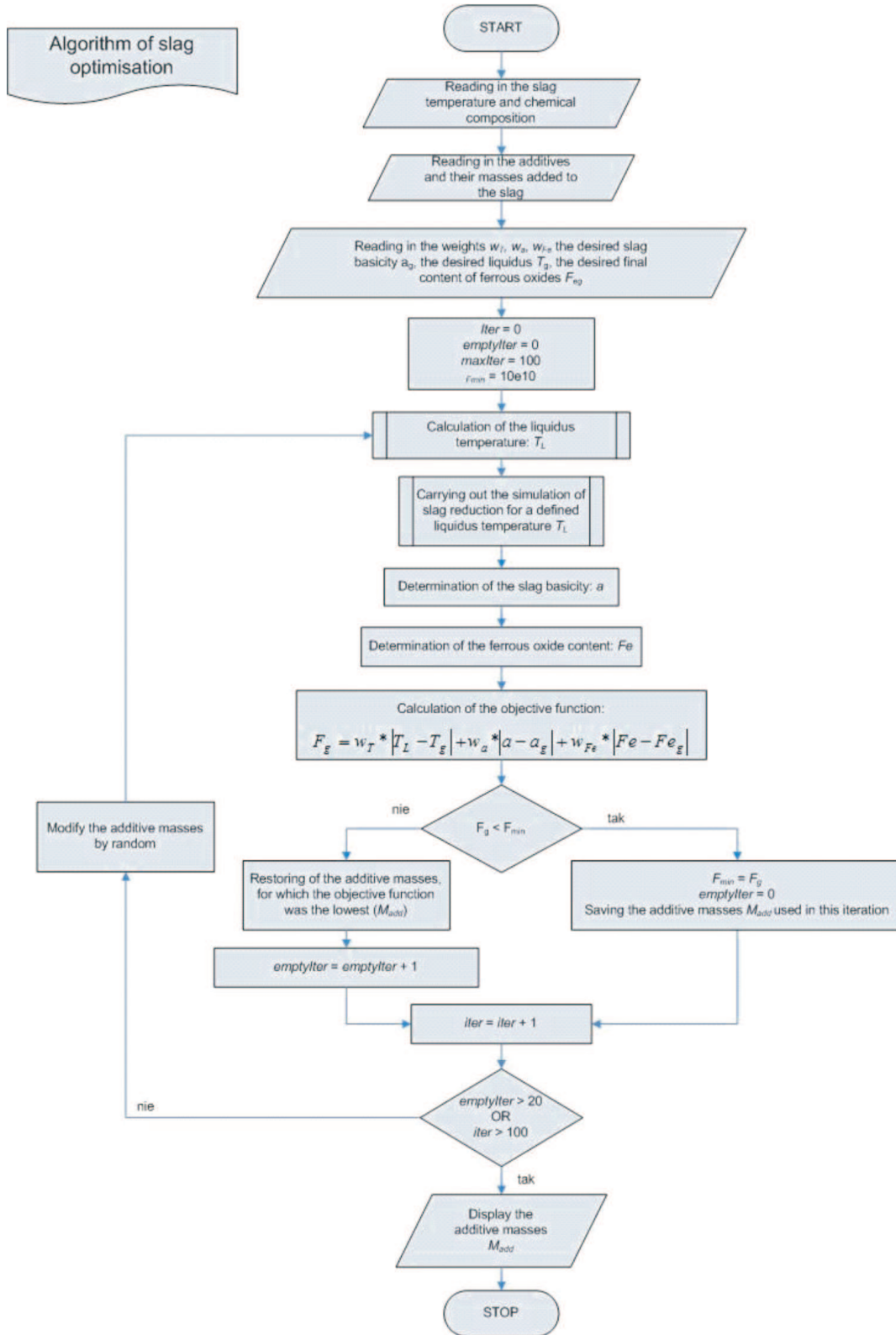
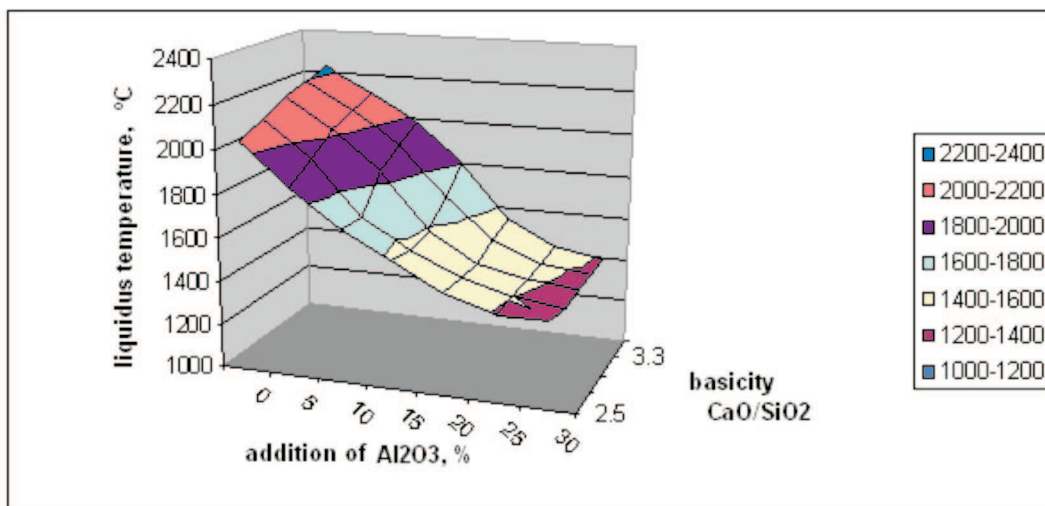Fig. 1. The algorithm for optimisation of the chemical composition of the charge for the slag reduction process

Fig. 2. The effect of the initial basicity of the slag reduced and the additive Al_2O_3 on the liquidus temperature of the reduced non-metallic phase
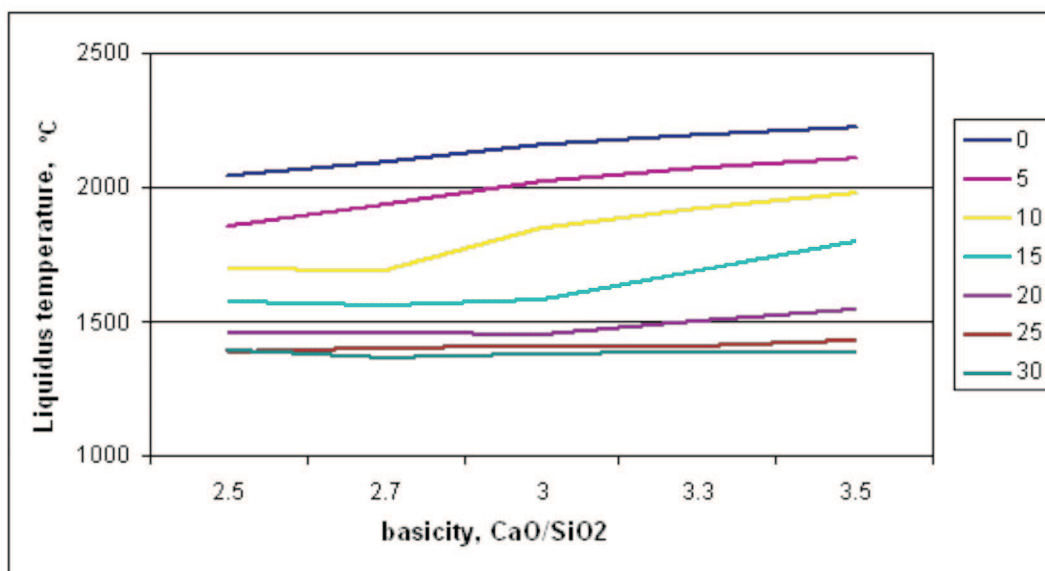

Fig. 3. The effect of BOF slag basicity on the liquidus temperature of the non-metallic phase after the reduction. The numbers in the legend box mean the percentage addition of Al_2O_3

6. Conclusion

The problem of steelmaking processes slag utilization is at the moment still an issue that requires the optimal solution. The difficulties in the utilisation of this waste arise from its chemical composition and physical characteristics. The main obstacle to its use in road construction is the need for seasoning or such processing that eliminates the negative effect of the volume change in the long term.

Therefore, the proposed process of slag reduction with modification of its composition seems a promising solution. As a matter of fact the present costs of such processing mean it is currently unviable, but this may change if the storage costs increase.

The conducted laboratory tests and model simulations confirmed the large controllability of the system understood as the possibility of obtaining a broad spectrum of chemical compositions of the material reduced and the variability of the liquidus temperature. The pro-

1112

posed optimisation procedure enables the requirements for the properties of the non-metallic phase obtained from the steelmaking slag reduction to be formed as one wishes.

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