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CHLORINATION OF NICKEL ORE BY GASEOUS CHLORINE IN THE PRESENCE OF ACTIVE ADDITIVES

I. Ilić, K. Cerović, S. Stopić and Ž. Kamberović*

The Faculty of Technology and Metallurgy, University of Belgrade
Karnegijeva 4, POB 3506, 11120 Belgrade, Serbia and Montenegro

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Abstract

Paper presents a thermodynamic analysis of chemical reactions occurring during chlorination with and without additives for both nickel oxides and nickel ferrites, which are component parts of nickel ore. The experimental research investigated the influence of temperature in the range from 600 up to 1000 °C and time (up to 3 h) on the chlorination degree of nickel ores with and without additives. It was found that the introduction of additives such as C, S, BaS and NaCl intensified the chlorination of nickel ore. The results can be applied and may help determine the optimal conditions for the chlorination of low-grade ferrous nickel ores.

Keywords: nickel ore, chlorine, chlorination, active additives

* ***Corresponding author:*** *kamber@elab.tmf.bg.ac.yu*

1. Introduction

Nickel lateritic ore are formed during lateritic weathering of ultramafic and mafic igneous rocks (peridotites, serpentinites, pyroxenites, and gabbros). Today, 40 % of the world Ni-production originates from, and 54 % of the total reserves are found in laterites [1]. Nickel processing from laterite ores is either performed by pyrometallurgical methods producing ferro-nickel, or by leaching with ammonia or sulphuric acid.

The chlorination processes by gaseous chlorine [2-4], hydrochloric acid [5,6], or halides of alkaline-earth metals [7,8] have a significant role in extractive metallurgy. The importance of chlorination lays in the exploitation of low-grade and complex raw materials and its further growth depends on new treatments, which more and more include the chlorination by gaseous chlorine or halides of alkaline-earth metals. Their high reactivity and strong affinity towards metal oxides and silicates enable the application field of halides and chlorine, in particular, to be expanded in metallurgy. Gaseous chlorine is one of the most aggressive chlorinating agents. However, certain minerals or compounds, as silicates or ferrites, are rather stable even towards elementary chlorine.

Nickel chloride pyrohydrolysis, the third major step-out technology driving the Goro (Serbia and Montenegro) Operation, allows for the production of nickel-oxide while regenerating hydrochloric acid for primary solvent extraction stripping [9]. Pyrohydrolysis is a technology that that has been used extensively by the steel industry for the treatment of pickle liquors and recovering iron.

The use of adequate additives can intensify the chlorination process. The influence of carbon being used as additive has been studied the most in the processes of selective chlorination of the mixture oxide row materials [9-11]. The influence of BaS, S and NaCl on the intensification and selectivity of chlorination has not been studied sufficiently [12-15].

The purpose of this paper is to study optimal conditions for selective chlorination of nickel pregnant ore aiming at the separation of nickel from other accompanying elements.

2. Experimental

The thermodynamic analysis has been made by using a HSC Chemistry software and its data base for thermodynamic values were required for the calculation of the standard Gibbs energy change (ΔG_T).

The chemical reactions for the chlorination of nickel silicate and nickel ferrite by chlorine with and without additives such as C, BaS, S and NaCl as well as their standard Gibbs' energy change at 298 K and 1173 K are shown in Tab.1.

Table 1. The Standard Gibbs' energy change at 298 K and 1173 K for chlornation reactions

Eq. No	Reaction	ΔG_{298}	ΔG_{1173}
1	$2\ NiO \times SiO_2\ (s) + 2\ Cl_2\ (g) = 2\ NiCl_2(s) + SiO_2\ (s) + O_2\ (g)$	-83.36	10.20
2	$2\ NiO \times SiO_2\ (s) + 2\ C + 2\ Cl_2\ (g) = 2\ NiCl_2(s) + SiO_2\ (s) + 2\ CO\ (g)$	-353.21	-420.74
3	$2\ NiO \times SiO_2(s) + BaS(s) + 3Cl_2\ (g) = 2\ NiCl_2(s) + SiO_2(s) + BaCl_2 + SO_2\ (g)$	-742.59	-532.94
4	$2\ NiO \times SiO_2\ (s) + 1/2\ S_2 + 2\ Cl_2\ (g) = 2\ NiCl_2(s) + SiO_2\ (s) + SO_2\ (g)$	-715.78	-276.53
5	$NiFe_2O_4\ (s) + 4\ Cl_2\ (g) = NiCl_2(s) + 2\ FeCl_3\ (g) + 2\ O_2\ (g)$	520.28	430.78
6	$NiFe_2O_4\ (s) + 3\ Cl_2\ (g) = NiCl_2(s) + 2\ FeCl_2\ (s) + 2\ O_2\ (g)$	156.25	175.96
7	$NiFe_2O_4\ (s) + 2\ C\ (s) + 3\ Cl_2\ (g) = NiCl_2\ (s) + 2\ FeCl_2\ (s) + 2\ CO_2\ (g)$	-645.24	-596.87
8	$NiFe_2O_4\ (s) + 2\ BaS\ (s) + 5Cl_2\ (g) = NiCl_2\ (s) + 2\ FeCl_2\ (s) + 2\ BaCl_2\ (s) + 2\ SO_2\ (g)$	-1230.50	-910.27
9	$NiFe_2O_4\ (s) + 2\ NaCl\ (s) + 1/2\ S_2\ (s) + 3\ Cl_2\ (g) = NiCl_2(s) + 2\ FeCl_2\ (s) + Na_2SO_4\ (s)$	-795.47	-473.95
10	$NiFe_2O_4\ (s) + 10\ FeCl_3\ (g) + 2\ BaS\ (s) = NiCl_2\ (s) + 12\ FeCl_2(s) + 2\ BaCl_2\ (g) + 2\ SO_2(g)$	-1186.23	-473.95

The affinity of metal oxides forming the ore with respect to chlorine can be represented in the following sequence:

$>SiO_2<Al_2O_3<Cr_2O_3<Fe_2O_3<MgO<FeO<NiO$.

So, it should be expected that, apart from nickel, FeO, MgO, Fe_2O_3, etc. are first to be chlorinated.

Silicate type of low-grade ferrous nickel ores taken from three different Yugoslavian sources (Rzanovo, Goles and Mokra Gora) were used in this study. Their chemical analyses are given in Tab. 2.

The granulometric distribution map of ore samples is shown in Fig. 1. The samples were 100% minus 200 mesh.

X-ray analysis of Rzanovo ore shows the presence of Fe_2O_3, Fe_3O_4, FeOOH, FeS_2, and SiO_2 .

The TGA-DTA analysis of the Rzanovo ore shows endothermic peaks at

250 °C, 410 °C, 875 and 1090 °C, confirming the removal of water, dissociation of FeOOH and dehidratation of talc and other Mg, Al hydrosilicates. Exothermic peaks at 455 °C, 700 °C, 960 °C represent transformation α- $Fe_2O_3 \rightarrow \gamma$ Fe_2O_3, crystallisation of olivine and transformation of Al-Si mineral structure.

Table 2. The Chemical analysis of ore

Element (phase)	Rzanovo % w/w	Goles % w/w	Mokra Gora % w/w
Fe	30.30	12.20	18.56
Fe_2O_3	26.10	17.20	19.48
FeO	4.20	0.20	6.05
SiO_2	27.57	56.63	39.11
Al_2O_3	4.79	2.50	6.30
MnO	0.26	0.20	0.30
Cr_2O_3	2.88	1.70	2.40
Ni	1.04	1.25	0.60
Co		0.04	0.04
MgO	0.75	5.25	11.50
CaO	9.67	0.25	0.80
TiO_2		0.03	0.03
S		0.04	0.10
CO_2	-	0.05	0.10
H_2O lost at 90°C	2.40	8.80	4.00
H_2O lost at 250°C		3.50	8.75
900°C lost	4.20		

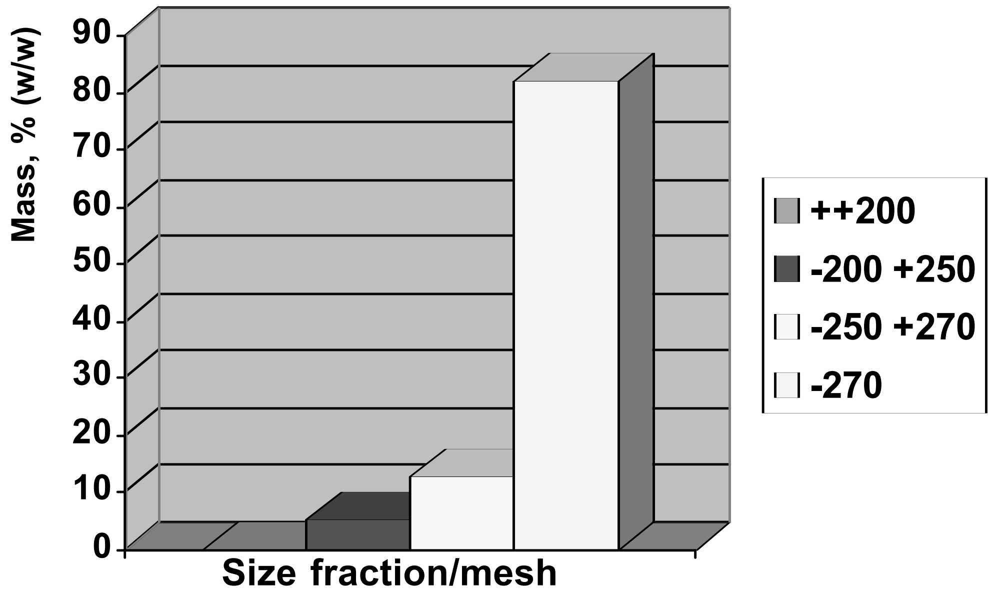

Figure 1. The granulometric distribution map of the ore samples

The coal with 100% coarseness of 63 μm and volatility of 40.65% from the locality of Kreka as well as a p.a. purity sodium chloride, barium sulphide and sulphur (Carlo Elba, Italy) with 100% coarseness of 63 μm have been used as additives.

The experiments of nickel ore chlorination by gaseous chlorine with and without the presence of added C, BaS, S and NaCl have been carried out in temperature range from 600 to 1000 ^{o}C and times up to 3 hours in order to determine the influence of temperature, time and present additives on the chlorination degree of nickel. The quantity of chlorine for the chlorination was one to three times larger than the stoichiometric one. The content of BaS amounted approximately 2 mass % with respect to the initial sample, and 1 mass % of coal or sulphur as additive.

The research was carried out in an electrically heated silica tube furnace in order to study the influence of various process parameters such as temperature, time and additives. Solid reactants were being introduced in a boat. The reactor was heated up to the investigated temperature before the samples were introduced. Gas flow was measured.

3. Results and Discussion

The overall chlorination degree of nickel and iron in dependence of time and temperature are shown in Figs. 2 and 3.

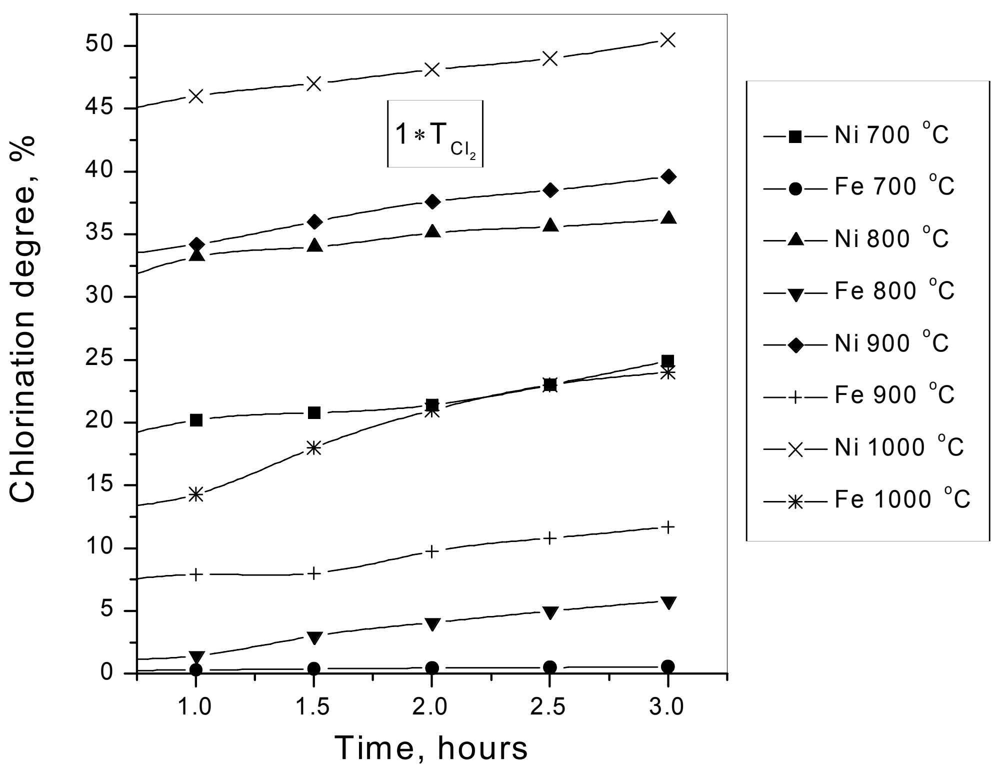

Figure 2. Dependence of the chlorination degree of Ni and Fe on temperature and time with theoretically quantity of chlorine for Rzanovo ore

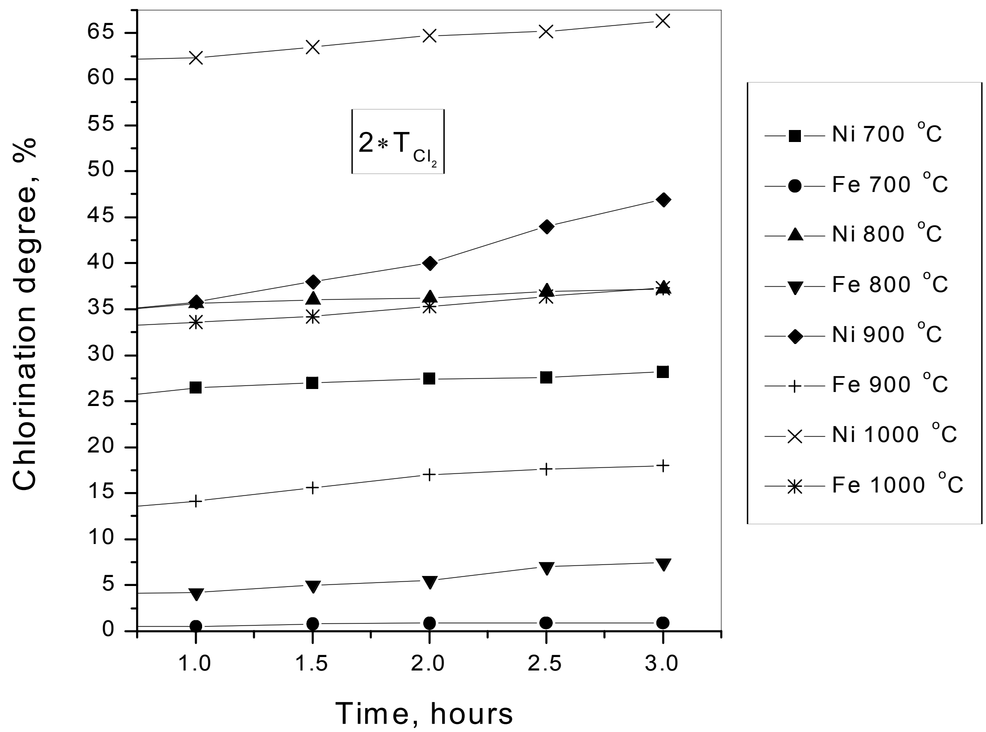

Fig 3. Dependence of the chlorination degree of Ni and Fe on temperature and time with quantity of chlorine two two times larger than the stoichiometric one for Rzanovo ore

As nickel is most probably bound in silicate and Ni-Fe spinnel forms, which are very stable, the chlorination degree of chlorine at the temperature of 1000 ^{o}C is 70%, whereas of Ni and Fe it is about 50%, for maximum temperatures and times and at the chlorine quantity, which is two times larger than the one theoretically required. The chlorination of Cr from the Rzanovo ore is low with the degrees from 0.5 up to 2.5. The dependence of the chlorination degree of nickel on the chlorine quantity is shown in Fig. 4.

At lower temperatures of 700-800 ^{o}C the influence of chlorine quantity on the chlorination degree of Ni and Fe is relatively low, whereas it is high at higher temperatures. The influence of chlorine quantity on the chlorination degree of Cr is minimal; i.e. there is no significant influence.

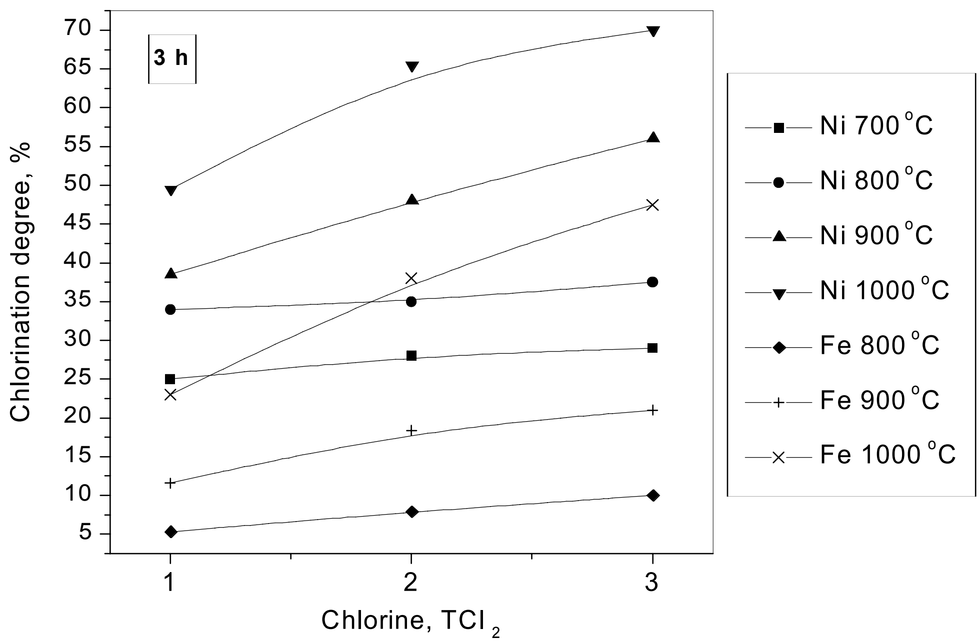

Fig 4. Dependence of the chlorination degree of Ni and Fe on the quantity of chlorine at the different temperature and time 3 h for Rzanovo ore

Fig. 5 shows the dependence of the chlorination degree of Ni, Fe and Cr on the quantity of coal at 800 ºC and the time of 1 hour.

The chlorination degree of Ni, Fe and Cr increases with the increase in the quantity of coal. The optimal degrees have been achieved with 8% of coal and therefore, this quantity has been taken as the optimal one in father investigation.

Fig. 6 shows the dependence of the chlorination degree of Ni and Fe with the theoretical quantity of chlorine on temperature and time

The results show that iron chlorinates approximately more than nickel and that this difference decreases with time. The chlorination degrees increase with the introduction of coal into the process. The chlorination degree of Fe increases more intensively than the chlorination degree of Ni, while the chlorination degree of Cr is still low and amounts up to the maximum of 6-7%.

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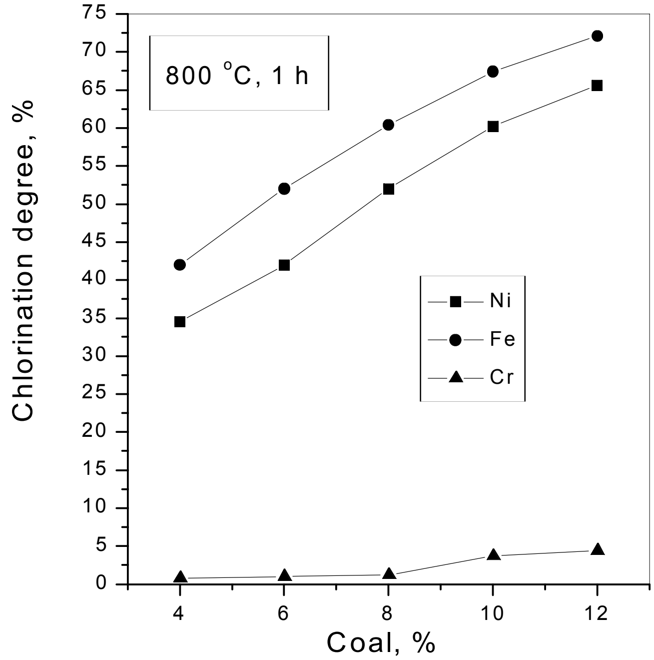

Figure 5. Dependence of the chlorination degree of Ni, Fe and Cr on the quantity of coal at 800 oC and 3 h for Rzanovo ore

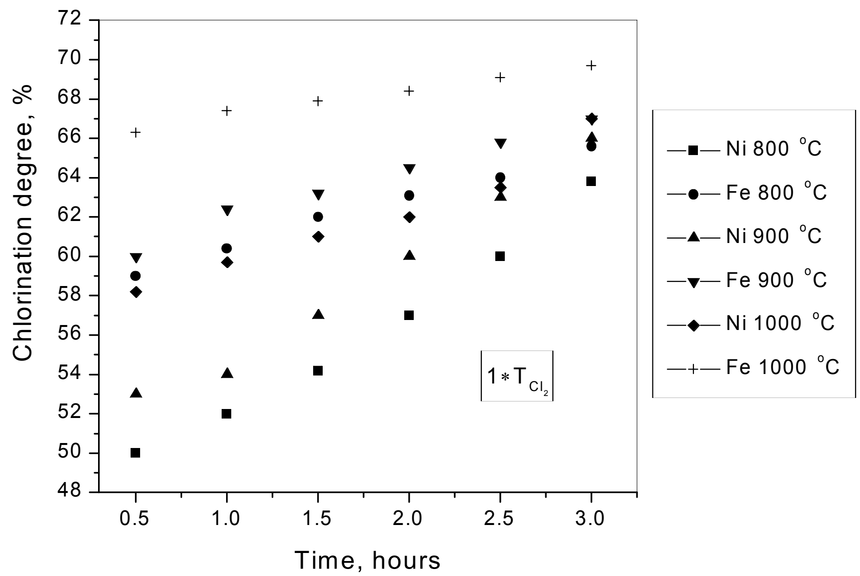

Figure 6. Dependence of the chlorination degree of Ni and Fe on temperature and time with stoichiometric quantity of coal for Rzanovo ore

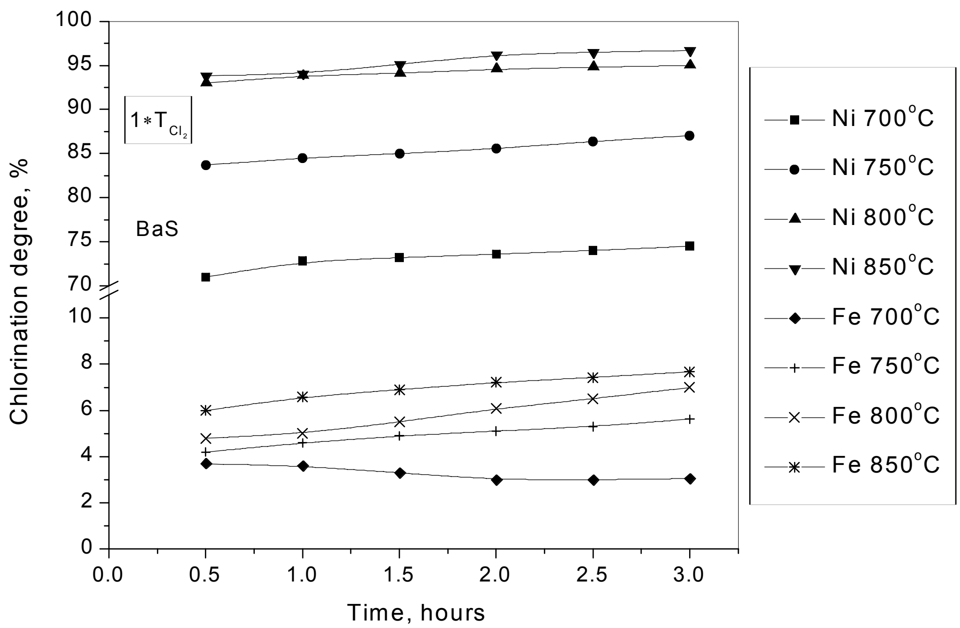

Figure 7. Dependence of the chlorination degree of Ni and Fe on temperature and time with BaS for Rzanovo ore

The results of the chlorination of the Rzanovo ore with quantity of chlorine is as theoretically required in the presence of BaS are shown in Fig. 7.

Based on the given results it can be concluded that the chlorination process develops fast and that there is no significant influence with time being prolonged for more than 1 h, even after 0,5 h except for Fe at the temperature of 700 °C. In the given conditions BaS chlorinates very fast, but at the same time the formed $BaCl_2$ makes it the diffusion of chlorine to Ni and oxides in the ore more difficult. The achieved chlorination degrees of Nickel are approximately 95% and of Fe from 4-8%.

The quantity of non-evaporated ferric chloride is relatively high with respect to the overall quantity of chlorinated Fe. The chlorination degree of Cr is low and amounts from 0.3 up to 3.3%.

Fig. 8 shows the chlorination results in the presence of NaCl and S.

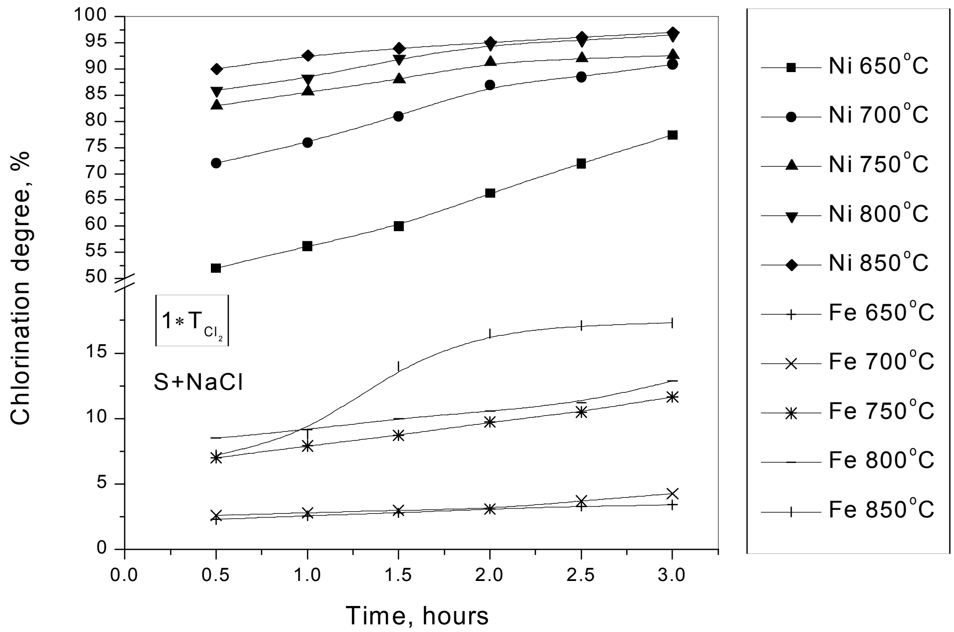

Figure 8. Dependence of the chlorination degree of Ni and Fe on temperature and time in the presence of S and NaCl for Rzanovo ore

Similar results are obtained as in the previous results with BaS. The temperature increase has insignificant influence on the chlorination degree at the temperatures above 800 ^{o}C.

Kinetics curves at low temperatures are somewhat different with respect to the curves for the chlorination with BaS. However, at high temperatures, similar kinetic dependence is obtained as in the chlorination with the addition of BaS.

In this case, a small chlorination degree of Fe is obtained at low temperatures, while chlorinated Fe is found in a solid form, mainly as $FeCl_2$. The quantity of ferric chloride increases with temperature and times the same as in the presence of BaS. The chlorination degrees of Fe are a little bit higher and range from 3-17%. The chlorination degree of Ni is high and ranges from 95-97%. The results show that the presence of S and NaCl do not affect the chlorination degree of Cr that ranges from 1.5-2%.

The comparison of the chlorination results of Ni, Fe and Cr in the presence of BaS and S+NaCl with the chlorination results obtained in the presence of added coal shows the following effects:

- high chlorination degrees of Ni;
- chlorination selectivity of Ni with respect to Fe and Cr;
- low consumption of chlorine with the higher chlorination degree of Ni that is 95%;
- chlorination temperatures are lower.

In order to verify the effects achieved in the chlorination of the Rzanovo ore in the presence of active additives, a study has been carried out to investigate the chlorination of silicate Fe and Ni ores from the Goles (Kosovo) and the Mokra Gora localities with additives.

Table 3. Influence of theoretically quantity of chlorine on the chlorination degree of Ni, Fe and Cr from Goles ore

Additive	Chlorination degree, %	750°C		850°C	
		Chlorination time, h		Chlorination time, h	
		1	3	1	3
BaS	Ni	79.06	-	91.55	-
	Fe	3.03	-	6.25	-
	Cr	4.10	-	4.20	-
S+NaCl	Ni	73.66	78.70	83.68	89.90
	Fe	2.86	3.75	3.90	5.28
	Cr	2.30	3.05	2.35	2.69

If the chlorination degrees of Fe and Ni from the Mokra Gora and Goles ores were compared with the Rzanovo ore, it can be seen that almost identical results in the chlorination degree have been obtained (the chlorination degree of Ni is 92-96%, of Fe is 4-8% and of Cr is 1-3%). The results show that the ferric chloride formed can occur as a chlorinating agent, which is in agreement with the thermodynamic analysis. The quantities of sublimed $NiCl_2$ in the chlorination with added BaS are lower. This can be explained by the formation of $BaCl_2$-$NiCl_2$ compound. Chromium practically does not chlorinate in any of the cases, and at the same time, the sintering of the samples has not occurred at the temperatures up to 900 °C.

Table 4. Influence of theoretically quantity of chlorine on the chlorination degree of Ni, Fe and Cr from Mokra gora ore

Additive	Chlorination degree, %	750°C		850°C	
		Chlorination time, h		Chlorination time, h	
		1	3	1	3
BaS	Ni	84.81	-	95.86	-
	Fe	7.38	-	8.20	-
	Cr	1.49	-	2.59	-
S+NaCl	Ni	80.75	84.60	94.07	96.15
	Fe	3.42	5.61	4.57	7.50
	Cr	1.75	2.40	2.22	2.40

4. Conclusion

The study of chlorination of Fe, Ni and Cr from Fe silicate Ni ores with the small nickel contact that amounted about 1%, from the Mokra Gora and the Goles localities confirm are in good agreement with previous investigations of the chlorination of Ni oxides [13-17], Ni silicates and Ni ferrites, as well as with theoretical study given in the thermodynamic analysis.

The optimal working parameters of the chlorination of Rzanovo ore without the presence of additives are the temperature of 1000 °C, three theoretical quantities of chlorine and time over 3 hours. In these conditions the chlorination degree of Ni is approximately 70%, of Fe is approximately 50%, and of Cr of approximately 3%. The similar results have also been achieved with the Mokra Gora and the Goles ores.

A very good chlorination selectivity of Ni with respect to Fe has been achieved in the chlorination of given ores in the presence of BaS and NaCl+S. The optimal conditions are the temperature from 800-850 °C , the time of 1 hour, and the chlorine quantity as theoretically required. The obtained chlorination results for Ni range from 93-96%, for Fe from 5-7%, and for Cr from 1-2%.

From the point of view of technological processing of these ores the results show the possibility of achieving a more favourable ratio of Ni with respect to Fe in chlorination products. At the same time, the consumption of chlorine is reduced as Fe chlorinates to a lower degree. The chlorination process of Ni is intensified and rather good selectivity achieved in this way.

In present conditions, the chlorination processes can be applied more easily and successfully by the use new materials and modern systems for automation and process control that are aimed at reducing the pollution of the environment. Future technologies for nickel processing will be based on hydrometallurgical processes.

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