

## PURIFICATION OF ZINC CONTAINING WAE LZ OXIDES FROM CHLORINE AND FLUORINE

Peter Iliev, Vladislava Stefanova, Biserka Lucheva, Dimitar Kolev

Department of Metallurgy of Non Ferrous Metals  
and Semiconductors Technology  
University of Chemical Technology and Metallurgy  
8 Kl. Ohridski, 1756, Sofia, Bulgaria  
E-mail: pkiliev@gmail.com

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### ABSTRACT

*The Waelz oxides (WO) obtained upon processing of zinc containing semi products in Waelz kilns are rich in impurities such as alkalines, chlorides and fluorides. After acid leaching of the WO chlorine and fluorine ions dissolve into the zinc electrolyte, causing corrosion of aluminum cathode and lead anode and sticking of the deposited zinc on the cathode. For normal production operation the WO must contain up to 1000 ppm chlorine and 100 ppm fluorine.*

*In the present study the laboratory tests on alkaline scrubbing of zinc containing WO in sodium carbonate solutions are presented. The effect of sodium carbonate concentration, pulp density and test duration on the degree of fluorine and chlorine purification is investigated. Based on the conducted research it was established that at temperature 363 K, pulp density 300 g l<sup>-1</sup>, concentration of sodium carbonate 100 g l<sup>-1</sup> and test duration 180 min, the final concentration of fluorine and chlorine in the treated WO is 90 and 220 ppm, respectively. WO with such concentration of impurities are appropriate for further processing for cathode zinc production.*

*Keywords:* Waelz oxide, alkaline scrubbing, fluoride, chloride.

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### INTRODUCTION

Upon autogenous smelting of lead concentrates applying Ausmelt technology (top submerged lance technology- TSL) at KCMAD a crude lead and furnace slag rich in lead and zinc are produced. Because of the high value of metal content the slag is not directly discarded but is treated in Waelz rotary kiln for metals recovery.

Waelz Rotary Kiln Process has found its application for processing of various zinc containing semi products (zinc-ferrite cakes, lead slags, pelletized electric arc furnace dust, etc.) due to its long history (more than a century) and established technology status (listed as Best Available Technology [1]). Inputs are TSL lead slag, coke breeze, binder (sand), electricity and gas. The process consists of reduction and volatilization of the non-ferrous metals in a rotary kiln [2 - 4]. The metals of interest (Zn, Pb, Cd) are reduced to their metallic state, sublimed into the free space of the furnace and

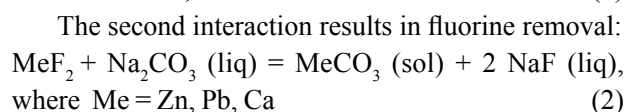
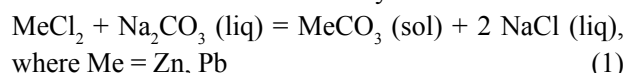
are finally reoxidized with an air current, obtaining an impure oxide with typical contents of about 50 % Zn, 10 % Pb and 0.25 % Cd, aside other impurities. These impure oxides are called Waelz oxide (WO). Unfortunately, the presence of certain elements, especially halogens, alkalines and sulfur, in the obtained WO forbids their use in electrochemical processes. For instance the fluoride ions content in the zinc electrolyte cause problems with the removal of the metallic zinc from aluminium cathode, while chloride ions attacks the lead anode, as well as chlorine gases may be formed and it can become a hazard to worker's health [5]. Thus, the maximum chlorine and fluorine concentration in the zinc electrolyte must be below 100 mg l<sup>-1</sup> and 50 mg l<sup>-1</sup>, respectively for the production of high quality zinc [6]. For this reason WO, are subjected to pre-treatment for impurities removal and then for zinc and lead recovery [7]. Currently two schemes for treatment of WO for impurity removal are applied: 1) oxidative roasting in

Table 1. Chemical composition of the impure WO, %.

Zn	Pb	Fe	Cd	CaO	SiO <sub>2</sub>	K	Na	Cu	Sb	F	Cl
55,6	18,4	0,5	0,45	0,5	0,35	0.38	0.28	0.036	0.12	0.037	0.80

multy-hearth furnace at 600 - 650°C; and 2) alkaline scrubbing in sodium carbonate solutions at 363 K. The second process is preferred due to its economic, energy and environmental effectiveness [8].

The alkaline scrubbing process is based on the next two chemical reactions. Firstly the sodium carbonate reacts with the metal chlorides by the interaction:



In the present research work the subject of experiments is impure WO obtained upon processing of TLS lead slag in Waelz rotary kiln. The aim of the laboratory experiments is purification of WO from chlorine and fluorine by alkaline scrubbing in sodium carbonate solutions. The effect of sodium carbonate consumption, pulp density and test duration on the degree of impurities removal is investigated. Single stage and two stage purification experiments are carried out.

## EXPERIMENTAL

### Methodology of the study

The laboratory apparatus for alkaline scrubbing of impure WO consists of a 1.0 L glass flask placed in a thermostat. The solution is stirred by means of a mechanical stirrer with rotation speed control. In order to limit evaporation, the reaction space is connected to a water-cooled reflux condenser.

After completion of the experiments the pulp obtained is filtered and the solid phase is desiccated at 353 K for 24 h and weighed on an assay balance. The concentrations of sodium and potassium in the treated WO are determined using a Perkin - Elmer 5000 atomic – absorption spectrophotometer and ICP–OES made by Prodigy. The concentrations of fluorine and chlorine are determined in the Central laboratory of KCM AD by means of ion selective pH meter (Metron).

### Chemical analysis of the impure WO

The chemical composition of the impure WO which is

a subject of the conducted research work is given in Table 1.

As can be seen from Table 1 the concentrations of chlorine (Cl) and fluorine (F) in the WO are over the technological limit of 1000 ppm Cl and 100 ppm F. Therefore purification step is necessary prior processing of WO for zinc production.

## RESULTS AND DISCUSSION

The goal of the alkaline scrubbing process is lowering of F and Cl content in the WO down to 1000 ppm Cl and 100 ppm F. WO with such concentration of impurities are appropriate for zinc production by electrowinning process. For this purpose the effects of temperature, reagent concentration, pulp density and test duration on the degree of F and Cl removal and their distribution between the solution and the treated WO is determined.

The laboratory experiments are conducted in two series: i) single stage scrubbing tests and ii) two stage scrubbing tests.

The test conditions and the obtained results on alkaline scrubbing of the impure WO produced upon processing of TSL lead slag in Waelz rotary kiln are presented in Table 2.

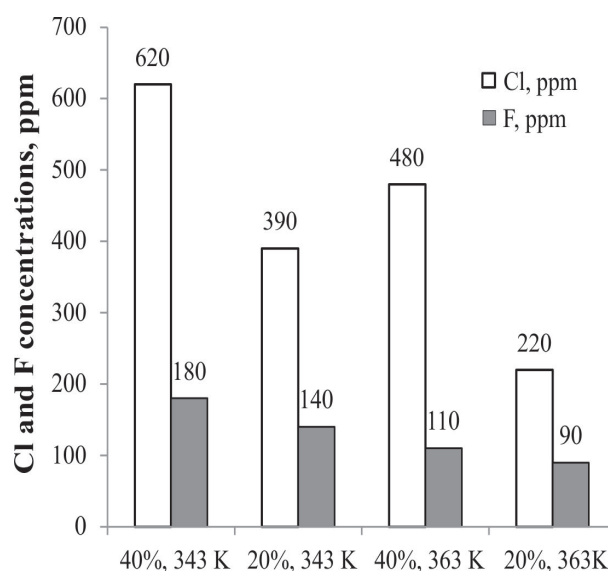


Fig.1. Effect of temperature on Cl and F concentration in the treated WO.

Table 2. Test conditions and experimental results on alkaline scrubbing of impure WO.

№	Treatment	Pulp density	$C_{Na_2CO_3}$ , g l <sup>-1</sup>	duration, h	Treated WO impurities content, %				Purification degree, %	
					Na, %	K, %	Cl, ppm	F, ppm	Cl	F
1*)	Single stage	1 : 2.5	100	3	1.42	0.11	620	180	92.25	47.05
2*)	Single stage	1 : 5	100	3	1.26	0.07	340	140	95.75	58.82
3	Single stage	1 : 2.5	100	1	1.61	0.06	900	120	88.75	67.57
4	Single stage	1 : 2.5	100	2	1.4	0.04	740	110	90.75	70.27
5	Single stage	1 : 2.5	100	3	1.31	0.04	480	110	94.0	70.27
6	Single stage	1 : 5	100	1	1.02	0.034	600	110	92.5	70.27
7	Single stage	1 : 5	100	2	1.12	0.03	220	100	97.25	72.97
8	Single stage	1 : 5	100	3	1.2	0.03	220	90	97.25	72.97
9	Single stage	1 : 2.5	50	3	1.14	0.04	570	160	92.88	56.75
10	Single stage	1 : 2.5	200	3	2.02	0.05	450	110	94.38	70.27
11	Single stage	1 : 5	50	3	1.0	0.02	300	120	96.25	67.57
12	Single stage	1 : 5	200	3	1.44	0.03	200	70	97.5	81.08
13	Single stage	3 : 10	50	3	0.94	0.022	340	120	95.75	67.57
14	Single stage	3 : 10	100	3	1.04	0.025	230	90	97.13	75.68
15	Single stage	3 : 10	200	3	1.29	0.027	230	70	97.13	81.08
16	Two stage	1 : 2.5	100	3+3	3.08	0.033	250	110	96.68	70.27
17	Two stage	1 : 5	100	3+3	3.66	0.03	250	100	96.68	72.97
18	Two stage	1 : 2.5	200	3+3	5.24	0.033	180	100	97.75	72.97
19	Two stage	1 : 5	200	3+3	3.68	0.046	200	60	97.5	83.78

\*) temperature 343 K

**Single stage experiments****Effect of the temperature**

The effect of this parameter on the degree of impurities removal is investigated at pulp density 20 % and 40 %, sodium carbonate concentration 100 g l<sup>-1</sup> and test duration 3 h. It is obvious from the results that the increase of temperature from 343 to 363 K has a positive effect on the degree of Cl and F removal (Fig. 1). With the increase of temperature the concentration of Cl in the treated WO declines from 640 to 480 ppm at pulp density 40 % and from 390 to 220 ppm at pulp density 20 %. With the rise of temperature the final content of F also decreases from 180 to 110 at pulp density 40 % and from 140 to 90 ppm for 20 % pulp density. Only at temperature 363 K the concentrations of Cl and F in the scrubbed WO are within the technological limits (up to 1000 ppm Cl and 100 ppm F). For this reason the rest of the experiments are conducted at that temperature.

**Effect of test duration**

The experiments of this series are carried out at temperature of 363 K and 100 g l<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> consumption. The rate of Cl and F removal at pulp density 20 % and 40 % are plotted on Figs. 2 and 3.

It can be concluded from the experimental data that

the final concentration of Cl decreases substantially with the prolongation of the test duration from 1 to 3 h, while the F content remains almost constant independently on the quantity of the solid phase in the sodium carbonate solution (pulp density). However the impurities content meets the technological requirements only upon scrubbing the WO at 20 % pulp density for 3 h.

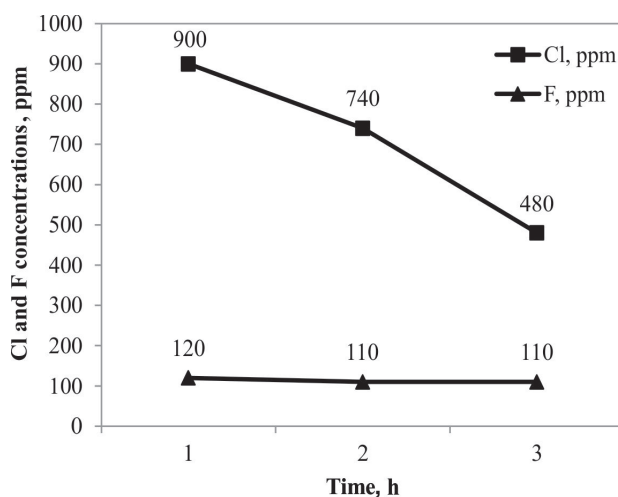


Fig. 2. Effect of test duration on Cl and F concentration in the treated WO at pulp density 40 %.

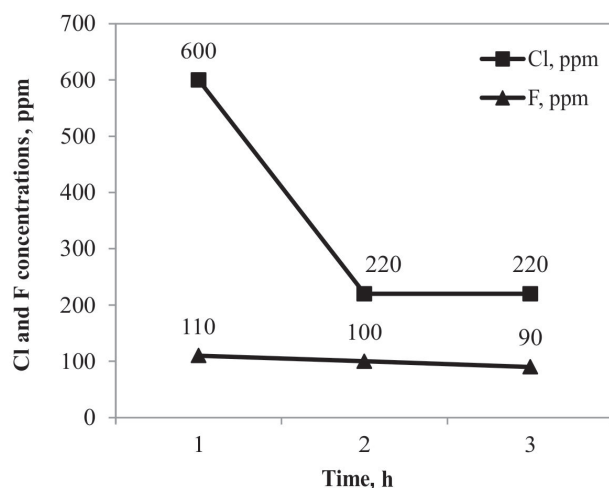


Fig. 3. Effect of test duration on Cl and F concentration in the treated WO at pulp density 20 %.

#### Effect of sodium carbonate concentration

The effect of that parameter on the extend of impurities purification is studied at 50, 100 and 200 g l<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> initial concentration, 20 %, 30 % and 40 % pulp density and temperature of 363 K. The test duration was 3h for all experiments. The final impurities content in the treated WO at different sodium carbonate concentrations is shown on Figs. 4, 5 and 6. As can be seen from the experimental results, the increase of reagent concentration results in decrease of impurities final content in the scrubbed WO. Nevertheless, treated WO with acceptable impurities content are obtained only at Na<sub>2</sub>CO<sub>3</sub> concentration of 100 g l<sup>-1</sup> or higher. However the rise of Na<sub>2</sub>CO<sub>3</sub> consumption also leads to increment of the process operational costs. The final pH of the scrubbing solutions was within the desired value of pH (10 - 10,5) just at 100 g l<sup>-1</sup> sodium carbonate initial concentration.

#### Effect of pulp density

The laboratory tests are conducted at 200, 300 and 400 g l<sup>-1</sup> solid phase (untreated WO) in the scrubbing solutions corresponding to 20, 30 and 40 % pulp density. The temperature and test duration are maintained constant during all experiments – 363 K and 3h, respectively. The effect of pulp density at different Na<sub>2</sub>CO<sub>3</sub> concentrations on the final impurities content is illustrated on Figs. 7, 8 and 9. As can be deduced from the experimental data the increase of pulp density (the amount of WO in the solution) leads to decrease of impurities purification degree regardless of the Na<sub>2</sub>CO<sub>3</sub> concentration. Thus, the scrubbing process should not be carried out at pulp density higher than 30 %.

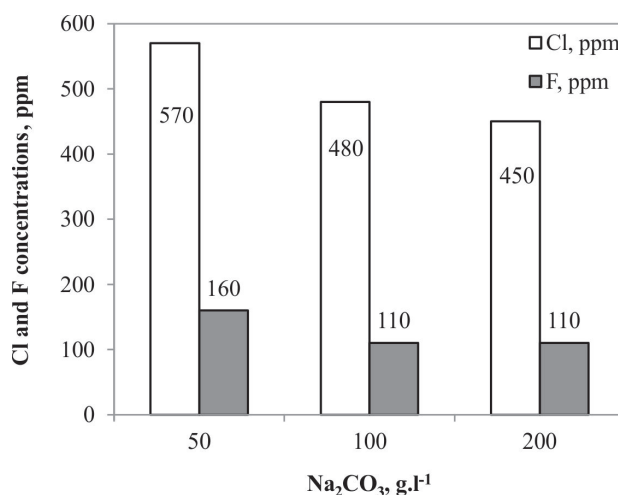


Fig. 4. Effect of sodium carbonate concentration on Cl and F content in the treated WO at pulp density 40 %.

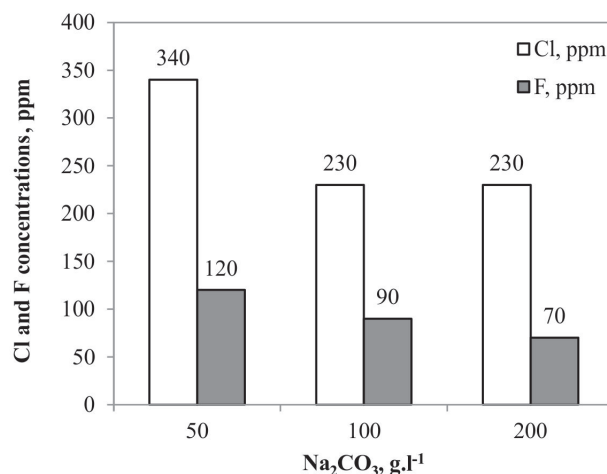


Fig. 5. Effect of sodium carbonate concentration on Cl and F content in the treated WO at pulp density 30 %.

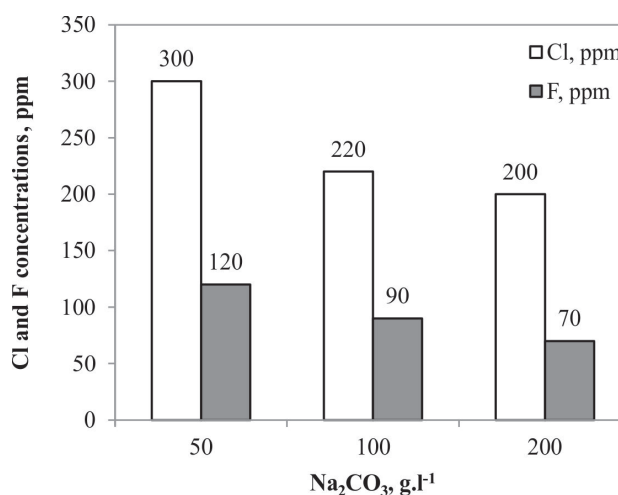


Fig. 6. Effect of sodium carbonate concentration on Cl and F content in the treated WO at pulp density 20 %.

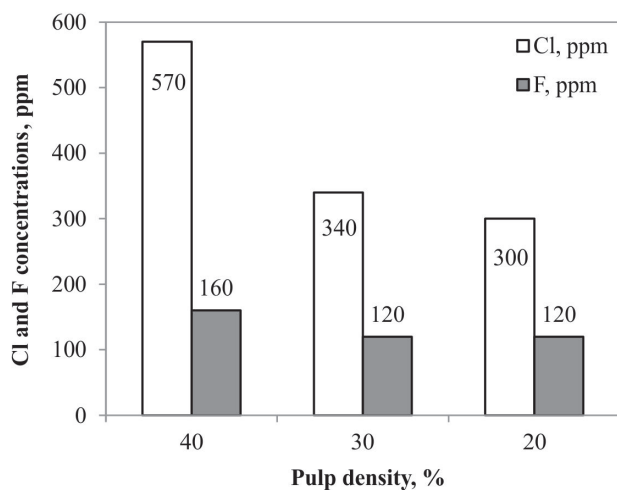


Fig. 7. Effect of pulp density on Cl and F content in the treated WO at sodium carbonate concentration of 50 g l<sup>-1</sup>.

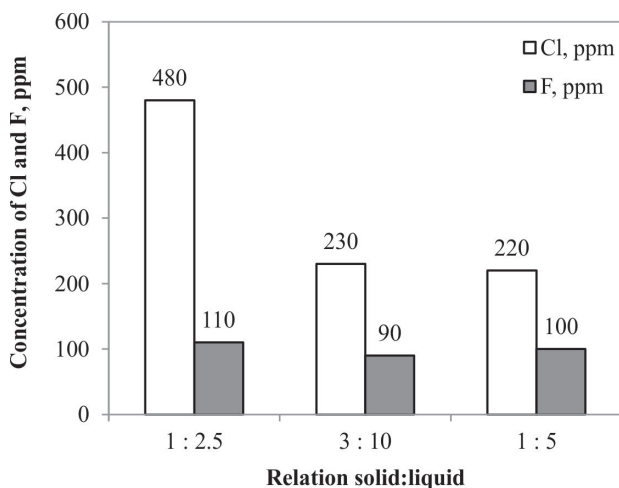


Fig. 8. Effect of pulp density on Cl and F content in the treated WO at sodium carbonate concentration of 100 g l<sup>-1</sup>.

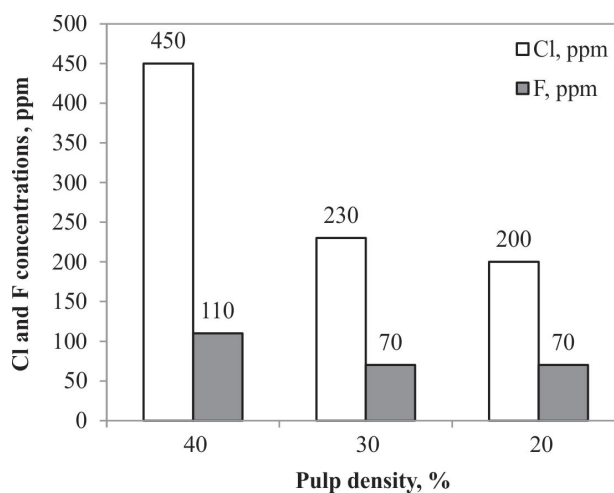


Fig. 9. Effect of pulp density on Cl and F content in the treated WO at sodium carbonate concentration of 200 g l<sup>-1</sup>.

### Two stage experiments

#### *Effect of pulp density and sodium carbonate concentration*

Two stage experiments are also carried out in order to investigate the possibility for deep purification of WO from impurities. The effect of the pulp density and sodium carbonate concentration on the chlorine, fluorine and sodium content in the treated WO is studied. During the tests the temperature is kept at constant level - 363 K. The test duration was 3 h for each of the two stages. After the first stage the pulp is filtered and washed with distilled water, then contacted with fresh sodium carbonate solution with the same initial concentration. After completion of the second stage the pulp is again filter and washed, than subjected to chemical analysis. The

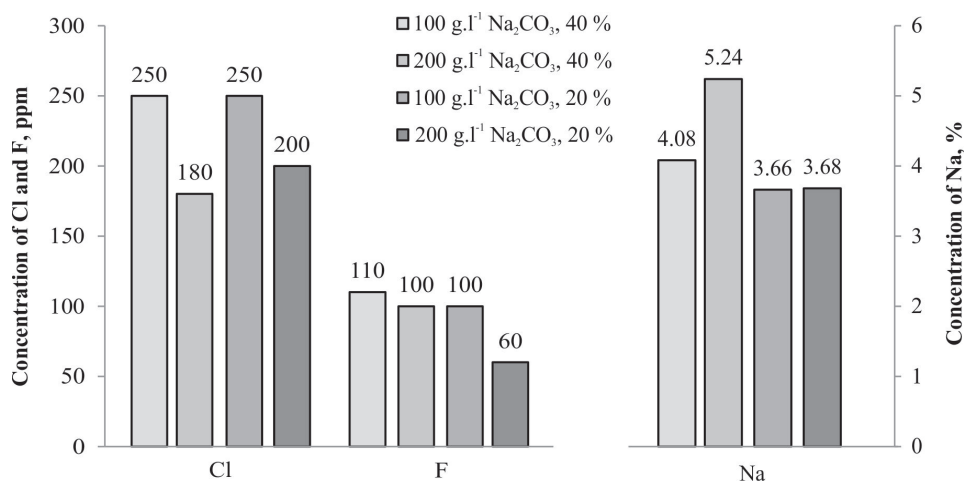


Fig. 10. Effect of pulp density and sodium carbonate concentration on Cl and F content in the treated WO.

effect of pulp density and sodium carbonate concentration on the final impurities content in the treated WO is depicted on Fig. 10. It is clear from the presented data that the two stage scrubbing process has a positive effect on the degree of chlorine and fluorine purification, but the sodium concentration in all samples of treated WO was over the technological limit of 2 % Na. For this reason the two stage scrubbing is rejected as an option for WO treatment.

## CONCLUSIONS

On the basis of the conducted research work the effect of the main technological parameters affecting the degree of contaminates removal from impure WO upon alkaline scrubbing is determined.

It is established that the optimal conditions of the process of single stage scrubbing should be carried out at temperature of 363 K, test duration 3 h,  $\text{Na}_2\text{CO}_3$  concentration 100 g l<sup>-1</sup> and pulp density 30 %. At these conditions 97,13 % of Cl and 75,68 % of F are removed from the WO and extracted in the alkaline solution. The obtained scrubbed WO are with concentration of impurities suitable for zinc production by electrowinning process.

The highest degree of chlorine and fluorine removal is obtained upon two stage treatment of WO at temperature 363 K, 200 g l<sup>-1</sup> sodium carbonate concentration and pulp density 20 % for 3 h duration of each stage (97,5 % of Cl and 83,78 of F). However the elevated sodium content in the double scrubbed WO (3,68 % Na) makes the two stage process inappropriate for this material.

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