

Recovery of tellurium from sodium carbonate slag

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Abstract: This study is devoted to tellurium recovery from sodium carbonate slag, formed in the fire refining process of crude silver. The slag was modified by silica additions and then reduced by carbon oxide. The degree of the slag modification was defined by the parameter k_W :

$$k_W = \frac{n_{SiO_2}}{n_{Na_2CO_3} + n_{Na_2O}}$$

where: n_i – the mole numbers of silica, sodium carbonate and sodium oxide.

The compositions of the investigated slag determined by the parameter k_W and the mole fraction of the tellurium oxide (x_{TeO_2}) are given in the following table.

Slag number	k_W	x_{TeO_2}
1	0.0	0.0622
2	0.2	0.0583
3	0.6	0.0526
4	1.0	0.4945

The reduction of tellurium was very fast for all the investigated slags, which was manifested by an almost complete conversion of CO into CO₂. Unfortunately, at the same time, a side reaction took place, and as a result sodium telluride was formed, which reported to the slag:



The tellurium content in the reduced slag decreases as the parameter SD increases, and only the slag with the SD equal unity was suitable for the tellurium recovery in form of dusts, containing more than 76 wt-% tellurium.

Keywords: tellurium recovery, crude silver, refining, sodium carbonate slag

1. Introduction

Tellurium was discovered at the end of eighteenth century in minerals containing gold. This metal is produced as a by-product of extraction of other metals (e.g. Cu, Ag, Ni, Pb etc). Some of copper, nickel, lead and silver deposits contain up to 5 ppm of tellurium. Tellurium is added in small quantities to steels for the improvement of their machinability and the preservation of fine grain. It is also used in cast iron production in order to stabilize the graphite

and iron carbide inclusions. Small tellurium additions to copper improves its machinability without markedly lowering its electrical conductivity. Te is also added to rubber in order to improve its resistance for aging.

Tellurium present in copper concentrates follow copper during its production, and in the copper electrorefining stage, it reports to slimes, which are raw materials for the precious metals (Ag, Au, Pt, Pd etc) recovery. In the Polish case, silver is the main precious metal recovered from these slimes. Tellurium is a harmful impurity of silver, which should be removed in the fire refining process below 100 ppm. This study is a part of the project devoted to tellurium removal from crude silver with the use of soda (Na_2CO_3) as the refining agent. It was found that the tellurium distribution coefficient ($L_{Te}^{slag/Ag}$) between the soda slag and the liquid silver at 1373 K does not depend on the oxygen pressure within the range (0.21 atm., 1 atm.), and is equal to 20.5. This study was aimed at the investigation of a possible method for tellurium recovery from the sodium carbonate slag.

2. Apparatus

The investigations of the tellurium reduction from the soda slag were carried out with the apparatus shown in Fig. 1. It consists of a furnace (1) in which an alumina crucible with the soda slag was placed. A stream of pure nitrogen with the flow rate of $20 \text{ dm}^3/\text{h}$ from cylinder (2) was passed through the reaction tube of the furnace. The nitrogen flow rate was controlled by an electronic flowmeter (6) and a controller module (7). Pure carbon monoxide and pure carbon dioxide were taken from the cylinders (3) and (4) and passed through the column (5) with magnesium perchlorate for the moisture removal. The flow rates of the carbon monoxide and carbon dioxide gases were also controlled by an electronic controller from Brooks (6) and a controller module (7). Next these gases were mixed in the column (8) filled with glass spheres. The CO-CO_2 mixture was passed by an alumina tube into the slag.

The gases generated by the reactions were passed through the filter (9) for the dust removal, and then were analyzed with an infrared gas analyzer (10) for the CO and CO_2 content. The obtained results were recorded by the computer (12). The sample's temperature was measured with a Pt-PtRh10 thermocouple and a Keitley (11) millivoltmeter. This thermocouple had been calibrated against the melting points of pure metals (Cu, Ag, Al, Zn, Sn).

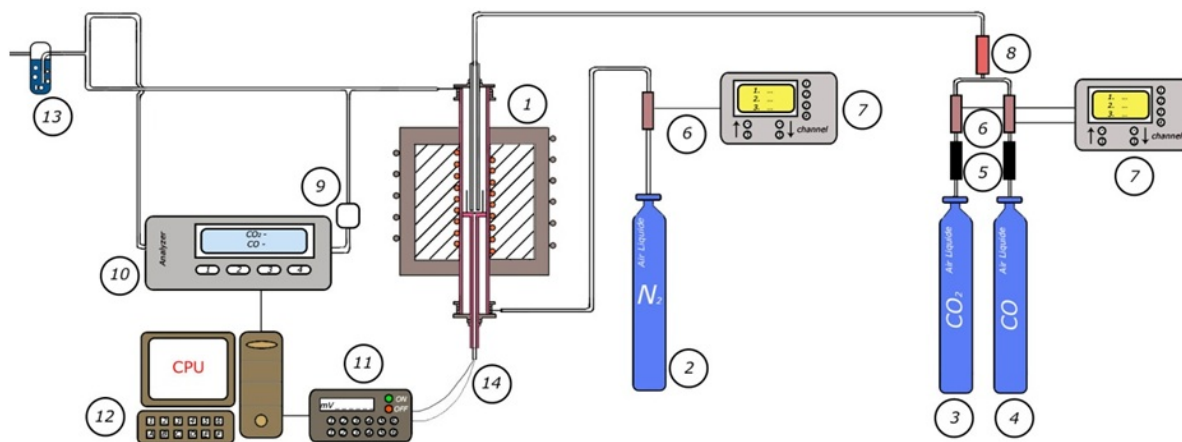


Fig. 1. Apparatus

3. Calibrations of the gas analyzer

The infrared gas analyzer used in this study is dedicated to analyze CO and CO₂ in their mixture. To speed up the passage of the reaction gases through the reaction tube, nitrogen of 25 dm³/h flow rate was admitted. For this reason, the gas analyzer had to be calibrated. The calibration was carried out by allowing a passage of a gas mixture containing nitrogen of 25 dm³/h flow rate with additions of predetermined flow rates of CO, CO₂, and CO+CO₂. The flow rates of these gases were controlled by Brooks flowmeters and corrected to 273 K. In consequence, the gas analyzer showed some readings for CO and CO₂ and the results were recorded by the computer. If the obtained reading of vol.-%CO and vol.-%CO₂ did not change with time, then these values were taken as true values. Figure 2 shows the relation between the gas analyzer readings for CO and the fraction of CO in the gas mixtures admitted into the reaction tube. A similar correlation was obtained for CO₂. It was assumed that the calibration data can be described by the relations:

$$A \cdot \frac{100 \cdot V_{CO}}{V_{N_2} + V_{CO} + V_{CO_2}} = \%CO \quad (1)$$

$$B \cdot \frac{100 \cdot V_{CO_2}}{V_{N_2} + V_{CO} + V_{CO_2}} = \%CO_2 \quad (2)$$

where: %CO, %CO₂ - the analyzer readings for CO and CO₂, respectively,

V_{CO} , V_{CO_2} - the flow rates of CO and CO₂ in [dm³/h],

A , B – the slopes of the calibration straight lines for CO and CO₂ respectively.

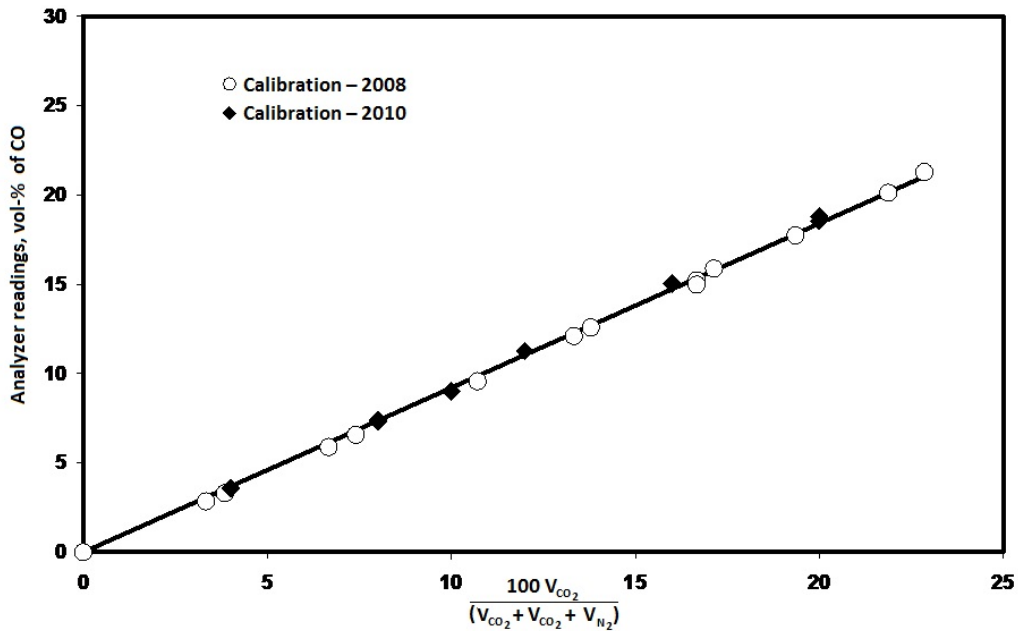


Fig. 2. Correlation between the readings of the gas analyzer for CO and the carbon oxide fraction in the gas mixture N₂-CO-CO₂ passing through the reaction tube of the furnace.

With the list squares methods and the calibration results, the “A” and “B” coefficients were determined:

$$(\%CO)_{real} = 1,058 \cdot \frac{100 \cdot V_{CO}}{V_{N_2} + V_{CO} + V_{CO_2}} \quad (3)$$

$$(\%CO_2)_{real} = 0,978 \cdot \frac{100 \cdot V_{CO_2}}{V_{N_2} + V_{CO} + V_{CO_2}} \quad (4)$$

Relations (3) and (4) were used for the determination of the flow rates of CO and CO₂ formed during the reduction process between two consecutive readings of the gas analyzer.

$$V_{CO} = \frac{20 \times (\%CO)}{92,01 - (\%CO) - 1,015 \times (\%CO_2)} \quad (5)$$

$$V_{CO_2} = \frac{20 \times (\%CO_2)}{90,59 - (\%CO_2) - 0,985 \times (\%CO)} \quad (6)$$

As the analyzer readings were adjusted to 273 K, the numbers of CO and CO₂ moles per one second could be calculated from the relations:

$$n_{CO} = \frac{V_{CO}}{22,4 \times 3600} \quad (7)$$

$$n_{CO_2} = \frac{V_{CO_2}}{22,4 \times 3600} \quad (8)$$

The number of oxygen moles removed from the slag during the period of 5 seconds was determined from the relation:

$$n_O^i = \frac{n_{CO}^i + n_{CO}^{i+1}}{2} \times 5 + 2 \times \frac{n_{CO_2}^i + n_{CO_2}^{i+1}}{2} \times 5 \quad (9)$$

where: n_{CO}^i , n_{CO}^{i+1} - the number of CO moles formed during the reduction process and calculated for two consecutive measurements,

$n_{CO_2}^i$, $n_{CO_2}^{i+1}$ - the number of CO₂ moles formed during the reduction process and calculated for two consecutive measurements.

4. Preliminary experiments

Despite a common view that sodium carbonate is an unstable compound, the CO₂ pressure for the equilibrium of the reaction (8) is quite low.



The equilibrium pressure of CO₂ for this reaction at the experimental temperatures is equal to: 0.66 Pa at 1373 K; 4.03 Pa at 1473 K and 20.62 Pa at 1573 K. To prevent the decomposition of the sodium carbonate, a mixture of 20 dm³/h of nitrogen and 1 dm³/h of CO₂ was admitted into the reaction tube. At these conditions two preliminary

experiments were conducted. These experiments consisted of two stages. The first stage was the melting of the sodium carbonate sample at 1373 K in the stream of the N_2 - CO_2 mixture. The second stage started after the thermal equilibration of the sample, and it consisted of alumina tube being immersed into the melt and a mixture of CO_2 - CO being passed through it. This mixture was made of streams of 1 l/h CO_2 and 4 l/h CO . In Fig. 2, the results of the first stage of the experiment are shown.

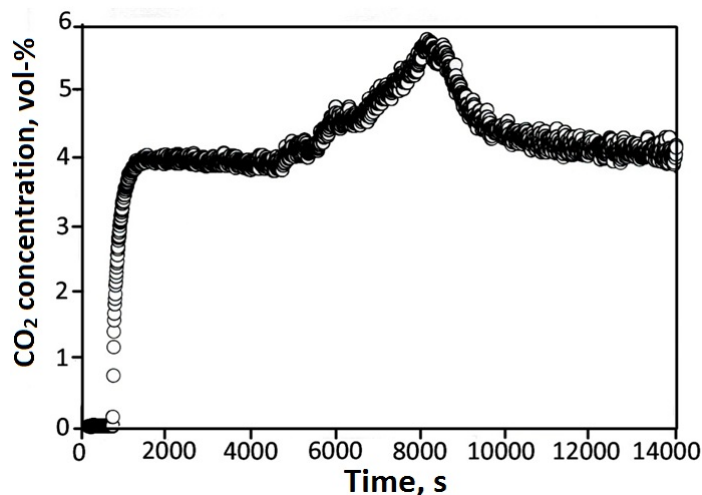


Fig. 3. Dependence of the CO_2 content in the N_2 - CO_2 mixture on time, during the temperature increase of the sodium carbonate sample up to 1373 K.

In the course of the sample heating, one can observe a noticeable increase of the CO_2 content above the incoming concentration in the N_2 - CO_2 gas. This CO_2 increase was observed at 1166 K, so it could be inferred that the soda was contaminated by some calcium carbonate. It was calculated that about 0.0069 CO_2 moles were additionally generated. In the second stage, after the thermal stabilization of the sample, the alumina tube was immersed into the melted soda, and the mixture of CO_2 - CO (1:4) was passed through the melt. The obtained results are demonstrated in Figure 4.

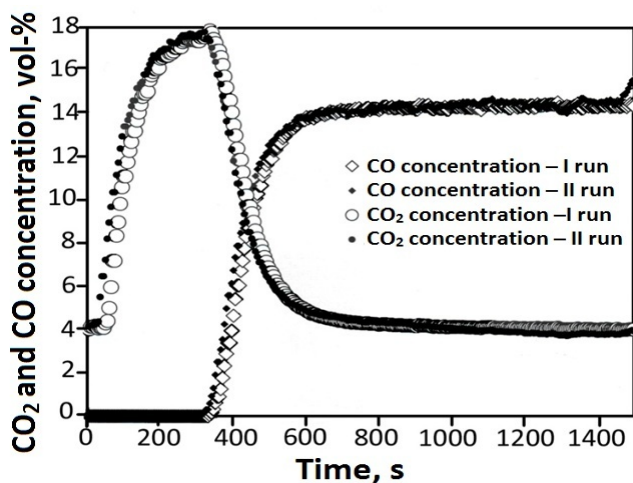


Fig. 4. Dependences of the CO_2 and CO contents in the reaction gas when passing the CO_2 - CO mixture (1:4) through the melted soda on time at 1373 K.

It was estimated that the numbers of the oxygen [O] moles removed from the slags was equal to 0.012 in the first trial and 0.013 in the second one. The obtained data suggest that the main soda impurities were CaO and CaCO₃. CaO is a very stable oxide, however the vapor pressure of calcium is relatively high at 1373 K, and can leave the reaction tube together with the CO-CO₂-N₂ mixture. Therefore calcium oxide can be reduced under the experimental conditions. In this work four slags were investigated, whose compositions were determined by the parameter k_W and the tellurium oxide mole fraction:

$$k_W = \frac{n_{SiO_2}}{n_{Na_2CO_3}} = \frac{n_{SiO_2}}{n_{Na_2CO_3} + n_{Na_2O}} \quad (11)$$

$$x_{TeO_2} = \frac{n_{TeO_2}}{n_{TeO_2} + n_{Na_2CO_3} + n_{Na_2O}} \quad (12)$$

Where: n_{SiO_2} ; $n_{Na_2CO_3}$; n_{Na_2O} ; n_{TeO_2} - the numbers of moles of silica, sodium carbonate, sodium oxide and tellurium oxide respectively.

It is worth mentioning that every slag contained exactly the same amount of tellurium. Table 1 contains compositions of these slags.

Table 1. Compositions of the investigated slag.

Number of slag	k_W	x_{TeO_2}
1	0	0.0622
2	0.2	0.0583
3	0.6	0.0526
4	1.0	0.4945

5. Results of the measurements at 1373 K for slag no 1 of the composition given by: $k_W = 0$ and $x_{TeO_2} = 0,0622$

This slag did not contain silica and had: 96.68 g of Na_2CO_3 and 11.942 g of the compound $Na_2O \cdot 2TeO_2$. After the careful mixing of these components, they were put into an alumina crucible which then was placed into the furnace. Next, the mixture of nitrogen with the flow rate of 20 l/h and carbon monoxide with the flow rate of 1 l/h was admitted into the furnace and the furnace was switched on. The temperature of the furnace was steadily increasing up to 1373 K. During this operation, the CO₂ concentration was monitored with the infrared gas analyzer. The obtained results are demonstrated in Fig. 5.

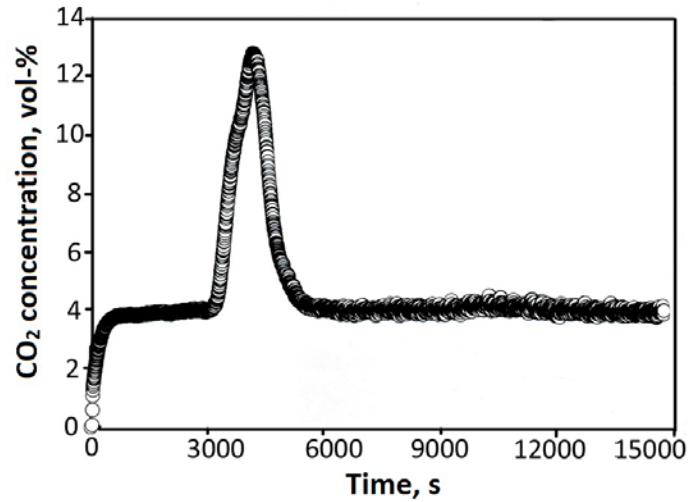
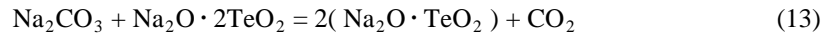


Fig. 5. Dependence of the CO₂ content in the gases leaving the furnace during the increase of the temperature of the sample up to 1373 K on time for the slag no 1.

A very rapid increase of CO₂ occurred when the sample temperature was within the range of 693 K – 783 K. Next, the concentration of CO₂ decreased to the initial value. The CO₂ peak can be the result of the reaction:



If this assumption is true, the number of the CO₂ moles should be equal to 0.031 under the experimental conditions. With the utilization of the experimental data presented in Fig. 5, it was calculated that an additional number of the CO₂ moles generated at this stage was equal to 0.027. As these numbers do not differ markedly, it is very likely that the assumption about the reaction (10) reflects reality.

When the sample achieved the experimental temperature (i.e. 1373 K) and the thermal equilibrium was reached, the alumina tube was immersed into the melt, and the CO – CO₂ (4:1) mixture was passed through the liquid sodium carbonate slag. The CO-CO₂ mixture was made of 4 dm³/h flow rate of CO and 1 dm³/h flow rate of CO₂. The outgoing reaction gas was analyzed for CO and CO₂, and the obtained results are presented in Fig. 6.

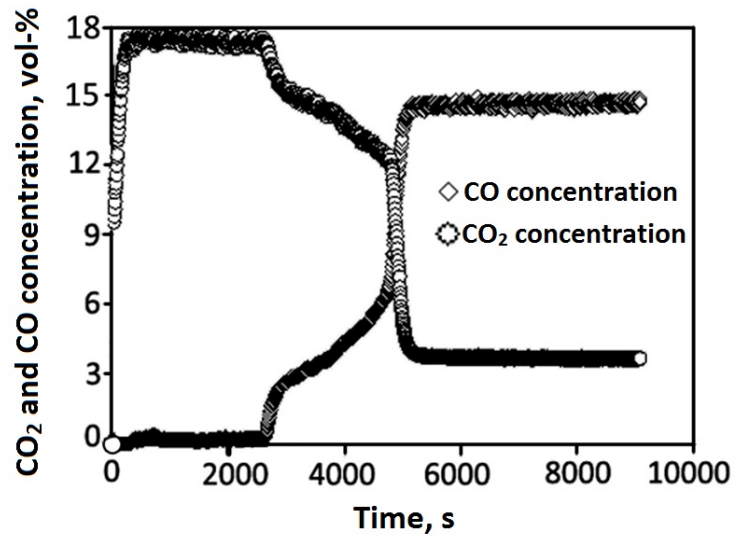
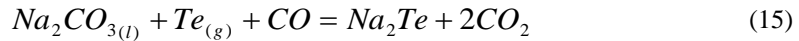


Fig. 6. Dependence of the CO₂ and CO content in the reaction gases on time, for slag no 1 at 1373 K in the second stage.

With the utilization of the experimental data shown in Fig. 6, the number of oxygen moles [O] removed from the slag was calculated and it equaled 0.1943. The process can be split up into two steps. In the first step, practically the whole CO is transferred into the CO₂, and the number of oxygen moles removed from the slag in this step equaled 0.1073. The second step is characterized by a steady decrease of the rate of the CO transformation into CO₂, and it is manifested by a decrease in the CO content and a simultaneous increase of the CO₂ concentration in the outgoing gas. In the second step, 0.0870 oxygen moles were removed from the slag. The TeO₂ present in the slag can give 0.1253 moles of oxygen if reduced completely according to the reaction:



The difference between the oxygen removed from the slag and that associated with TeO₂ is equal to 0.0690 moles. However, the chemical analyses of the slag after the experiment with a spectrometer OPTIMA 7300DV of PerkinElmer, revealed that the tellurium concentration equaled 7.23 wt-%, while the preliminary tellurium content in this slag before the experiment was 8.09 wt-%. The question is, how to explain these contradictory facts, and could it be reconciled by the assumption that the following reaction takes place:



Under this assumption, additional oxygen should be generated, and in the case when the whole tellurium is reduced, 0.0627 moles of oxygen [O] could be additionally removed from the slag. In consequence, 0.1880 moles of oxygen altogether (0.1253 + 0.0627) should be removed from the slag, if the whole tellurium present in the initial slag takes part in the reactions (11) and (12). The difference between the amount of the oxygen removed from the slag calculated from the experimental and the theoretical data (0.1943 – 0.1880 = 0.006) is quite small and equals only 3.3 %.

6. Results of the measurements at 1373 K for the slag no 4 of the composition given by: $k_w = 1$ and $x_{TeO_2} = 0,04945$

This slag contained the most of silica and in consequence, the obtained results differ very much from those for the slag without silica ($k_w = 0$). This slag was made of 36.179 g of SiO₂; 60.500 g of Na₂CO₃ and 11.942 g of the compound Na₂O·2TeO₂. After the careful mixing of these components, they were put into an alumina crucible, which then was placed into the furnace. Next, the mixture of nitrogen with the flow rate of 20 l/h and carbon monoxide with the flow rate of 1 l/h was admitted into the furnace and next, the latter was switched on. The temperature of the furnace was steadily increasing up to 1373 K. During this operation, the CO₂ concentration was monitored with an infrared gas analyzer. The obtained results are demonstrated in Fig. 7.

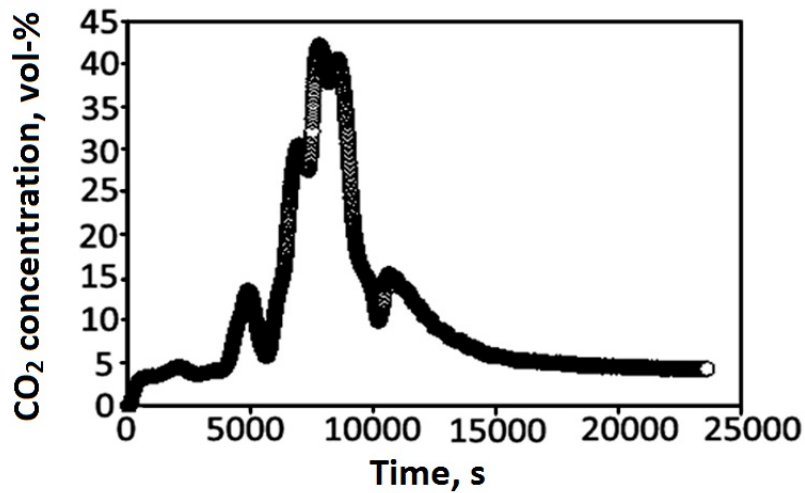
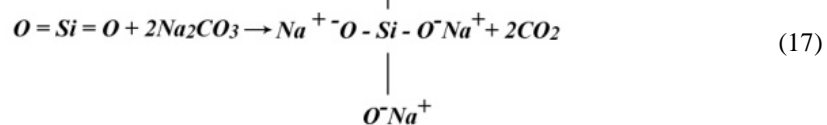
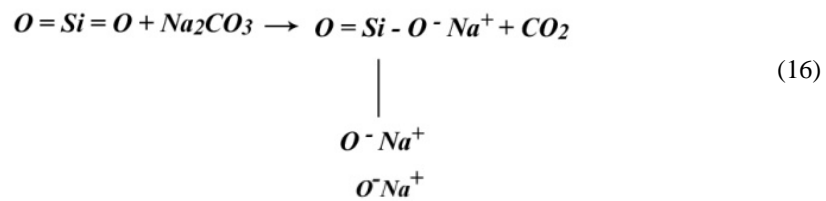


Fig. 7. Dependence of the CO₂ concentration in the outgoing gases on time, during the increase the temperature of sample no 4 up to 1373 K.

As it can be seen, this dependence exhibits a few maxima and minima, which can be explained schematically by the reactions:

The melted soda dissolves the silica, and the reactions of its depolymerization take place according to the reactions:



The slag depolymerization proceeds as the temperature increases, as the equilibrium of the reactions (13) and (14) is shifted to the right side. The calculation revealed that 0.4831 moles of CO₂ were removed from the slag at this stage. In consequence, the composition of the slag at the end of this stage was the following: $n_{SiO_2} = 0.6021$; $n_{Na_2CO_3} = 0.0099$; $n_{Na_2O} = 0.5457$; $n_{TeO_2} = 0.0626$. When the sample achieved the experimental temperature (i.e.1373 K) and the thermal equilibrium, the alumina tube was immersed into the melt, and the CO – CO₂ mixture (4:1) was passed through the liquid sodium carbonate slag. The CO-CO₂ mixture was made of 4 dm³/h flow rate of CO and 1 dm³/h flow rate of CO₂. The outgoing reaction gas was analyzed for CO and CO₂, and the obtained results are presented in Fig. 8.

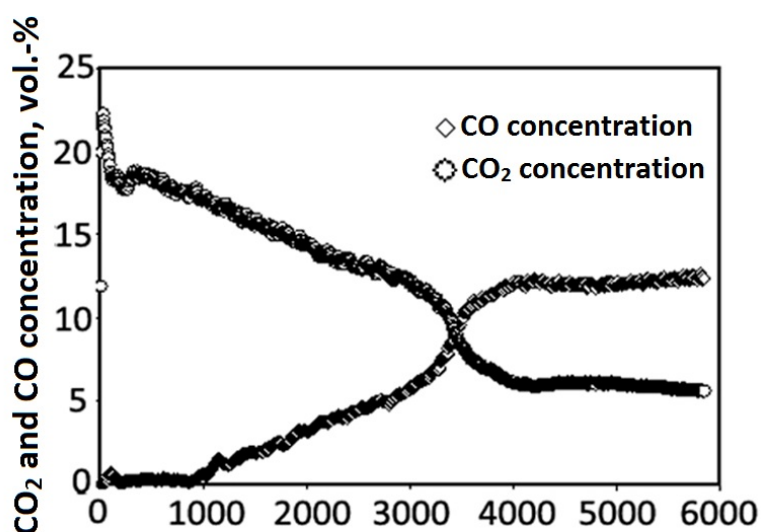


Fig. 8. Concentrations of the CO and CO₂ changes versus time, during the passing of the CO-CO₂ mixture (1:4) through slag no 4, at 1373 K.

With the utilization of the experimental data presented in Fig 8, the number of the moles removed from the slag was calculated as 0.1498. It means that from this slag, (no 4) 0.0245 moles of oxygen more were removed than those associated with TeO₂. The chemical analyzes of this slag after the reduction stage showed 1.23 wt-% of tellurium in it. It means that the majority of the reduced tellurium did not form sodium telluride. The following question should be asked: What caused such behavior? It is worth mentioning that this slag, after melting, contained a very small amount of soda (~0.01 moles of Na₂CO₃ at 1373 K). This suggests that the Na₂O is very strongly bonded within the silicate polyionic and therefore cannot react with the reduced tellurium to form sodium telluride. Therefore it seems that sodium carbonate serves as a sodium supplier for the reaction of the sodium telluride formation. The investigation results obtained at 1373 K; 1473 K and 1573 K are given in Tables 2, 3 and 4.

Table 2. Results of the investigation on the tellurium recovery from the sodium carbonate slag at 1373 K.

<i>kw</i>	Mole numbers of the slag components before reduction stage				Oxygen [O] removed in reduction stage, moles	Te content after reduction stage, wt-%
	Na ₂ CO ₃	SiO ₂	Na ₂ O	TeO ₂		
0	0,8808	0,0000	0,0626	0,0626	0,1943	7,23
0,2	*0,5107	0,1694	*0,3366	0,0626	0,1438	6,99
0,6	*0,1186	0,4224	*0,5852	0,0626	0,1630	6,76
1,0	*0,0099	0,6021	*0,5457	0,0626	0,1498	1,23

* - Mole numbers estimated from the experimental data of CO₂ removed from the slag during the melting stage.

Table 3. Results of the investigation on the tellurium recovery from the sodium carbonate slag at 1473 K.

<i>kw</i>	Mole numbers of the slag components before reduction stage				Oxygen [O] removed in reduction stage, moles	Te content after reduction stage, wt-%
	Na ₂ CO ₃	SiO ₂	Na ₂ O	TeO ₂		
0	0,8808	0,0000	0,0629	0,0626	0,1924	7,39
0,2	*0,4834	0,1694	*0,3640	0,0626	0,1924	8,34
0,6	*0,0738	0,4224	*0,6171	0,0626	0,1844	8,40
1,0	*0,0133	0,6021	*0,5988	0,0526	0,1537	1,76

* - Mole numbers estimated from the experimental data of the CO₂ removed from the slag during the melting stage.

Table 4. Results of the investigation on the tellurium recovery from the sodium carbonate slag at 1573 K.

<i>kw</i>	Mole numbers of the slag components before reduction stage	Oxygen [O]	Te content
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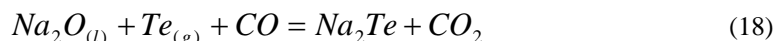
	Na_2CO_3	SiO_2	Na_2O	TeO_2	removed in reduction stage, moles	after reduction stage, wt-%
0	0,8808	0,0000	0,0629	0,0626	0,1660	8,74
0,2	*0,4664	0,1694	*0,3810	0,0626	0,1670	9,37
0,6	*0,0569	0,4224	*0,6470	0,0626	0,1568	7,86
1,0	*0,0727	0,6021	*0,5294	0,0626	0,1233	2,25

* - Mole numbers estimated from the experimental data of the CO_2 removed from the slag during the melting stage.

7. Discussion

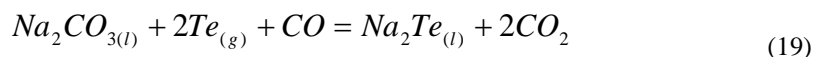
The experimental results obtained in this work suggest that in every case, a complete extraction of tellurium from the slags should be expected. This conclusion is supported by the fact that in every case, the amount of the oxygen removed from these slags exceeded the oxygen connected with TeO_2 . Since the tellurium vapour pressure at the experimental temperatures is quite high ($P_{Te}(1373K) = 800 Pa$, $P_{Te}(1473K) = 2330 Pa$, $P_{Te}(1573K) = 5846 Pa$) [1], so the tellurium should report to dust. The chemical analyzes of the slags after the reduction stage showed that almost all the tellurium remained in it, with the exemption of the slag with $k_W = 1$. In the cases of the slag with $k_W = 1$, most of the tellurium was reduced. There are two possible mechanisms which can explained such behavior:

1. The reduced tellurium reacts with the sodium oxide according to the reaction:



The equilibrium constants of the reaction (15) at the experimental temperatures are very high ($K_{1373} = 8.587 \cdot 10^7$; $K_{1473} = 6.661 \cdot 10^6$; $K_{1573} = 6.553 \cdot 10^5$) [1].

2. Reduced tellurium reacts with sodium carbonates according to the reaction:



The equilibrium constants of the reaction (16) at the experimental temperatures are much smaller ($K_{1373} = 562,8$; $K_{1473} = 264,8$; $K_{1573} = 133,4$) [1].

Let us assume for a moment that the sodium telluride is formed according to the reaction (15). In such case with the increase of the parameter k_W , the tellurium content in these slags should also increases. In fact, a very small increase is observed for the small values of k_W , however, for higher values of the parameter k_W , the tellurium content in the slags markedly decreases. It means that the reaction (16) plays the main role in the reaction of the sodium telluride formation. It is very likely that the sodium oxide is bonded very strongly within the silicate polyionic and therefore cannot react with the reduced tellurium to form sodium telluride. In other words, the tellurium recovery from the slag would be possible in the case when almost all the sodium oxide were tied up with the silicate polyionic ($k_W \geq 1$). As the temperature increases, the silicate polyionic becomes less stable and therefore a higher tellurium concentration in the slag with the parameter $k_W = 1$ is observed (see Fig. 9).

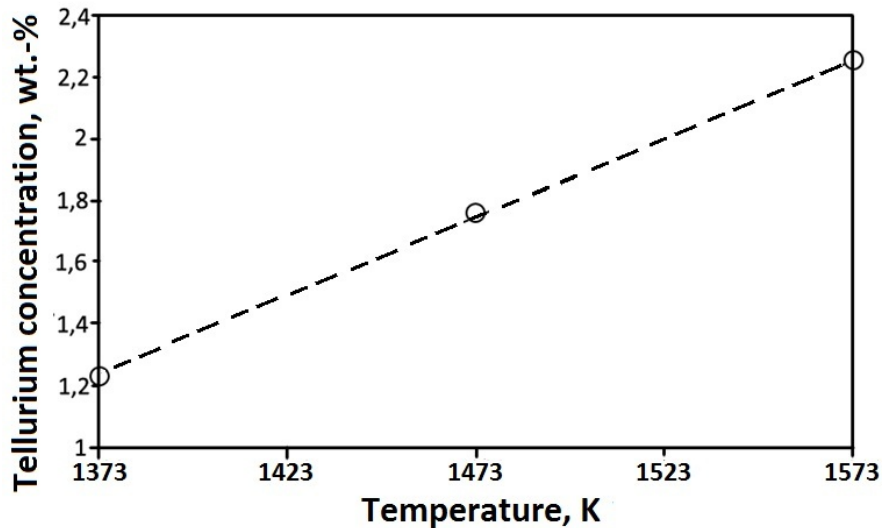


Fig. 9. Tellurium content in the slag with $kw = 1$ after reduction as a function of temperature.

The results of this work give a clear prescription for how to recover tellurium from the sodium carbonate slag. It is necessary to add some silica to such a slag in order to set up the parameter kw value higher than unity. The temperature of the process should equal 1373 K or even lower. To support this opinion, an additional experiment was carried out for the slag of the composition given by:

$$kw = \frac{n_{SiO_2}}{n_{Na_2O} + n_{Na_2CO_3}} = 2 \quad x_{TeO_2} = \frac{n_{TeO_2}}{n_{TeO_2} + n_{SiO_2} + n_{Na_2O} + n_{Na_2CO_3}} = 0,0335$$

As the silica concentration was high, the experiment was conducted at 1473 K. The tellurium concentration in this slag after the reduction stage was as low as 0.1%. The reduced tellurium reports to dust, because of the high pressure of this metal at elevated temperatures. Fig. 10 shows the obtained dusts containing more than 76 wt-% of tellurium.



Fig 10. Obtained dusts containing more than 76 wt-% Te.

Acknowledgments

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