



Selective recovery of uranium from Ca-Mg uranates by chlorination



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HIGHLIGHTS

- The chlorination is an effective method for the recovery uranium from Ca-Mg uranates.
- The optimal conditions were: 10 hs of reaction time at 700 °C using 3 l/h of Cl₂(g).
- U₃O₈ is recovery by washing out the chlorination by-products.

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ABSTRACT

A chlorination process is proposed for the uranium extraction and separation using Calcium–Magnesium uranates such as starting reactants which were obtained by precipitation from uranyl nitrate solutions with calcium hydroxide. The study is based on thermodynamic and reaction analysis using chlorine gas as chlorination agent. The results showed that the chlorination reaction of Ca uranate is more feasible to occur than the Mg uranate. The products obtained after chlorination reactions were washed with deionized water to remove the chlorides produced and analyzed. The XRD patterns of the washed products indicated that the chlorination between 400 and 500 °C result in a single phase of calcium uranate (CaUO₄) as reaction product. The formation of U₃O₈ and MgU₃O₁₀ was observed at temperatures between 600 °C and 700 °C for 8 hs. The optimal conditions to recover uranium were 3 l h⁻¹ of chlorine and 10 hs of reaction at 700 °C being U₃O₈ the single uranium product obtained.

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1. Introduction

Increasing depletion of high-grade uranium ores and the necessity of reuse radioactive solid wastes have resulted in an increasing demand of new processes for the efficient extraction of uranium from solids wastes and minerals [1–4]. Many precipitated solids are obtained in uranium plants, such as uranium enrichment or conversion of UO₂ to UF₆ plants [5,6]. This is due to uranium capture systems with alkaline or alkaline earth cations which generate precipitates that constitute a nuclear waste. Ca²⁺ is a cation used in precipitation system, for example in capturing currents of UF₆ or other uranium volatile compounds. Alkaline earth uranates have usually the general formula Me_xUO_{x+3}.

In order to retrieve and extract uranium from solid wastes

formed by mixtures of compounds, it is necessary to find an effective method. The extraction of uranium from solid precipitates and contaminated soils can be carried out through chlorination techniques which can be a way for the preparation of high purity materials [2,3,7–10].

The present article consists of a first part which is a thermodynamic study of the complete chlorination process. According to this, all steps are thermodynamically possible and the optimum process parameters are discussed. The results indicate that the most problematic parts of the process are the complete chlorination of CaUO₄ without formation of uranium chlorides and the chlorination of Mg uranates. Therefore, the second part of this work is dedicated to the experimental study of the chlorination step. The influence of the working temperature was investigated in order to determine the optimal process conditions providing complete chlorination with separation of U₃O₈. The conditions were set to provide complete chlorination, but preventing volatilization of the uranium compounds.

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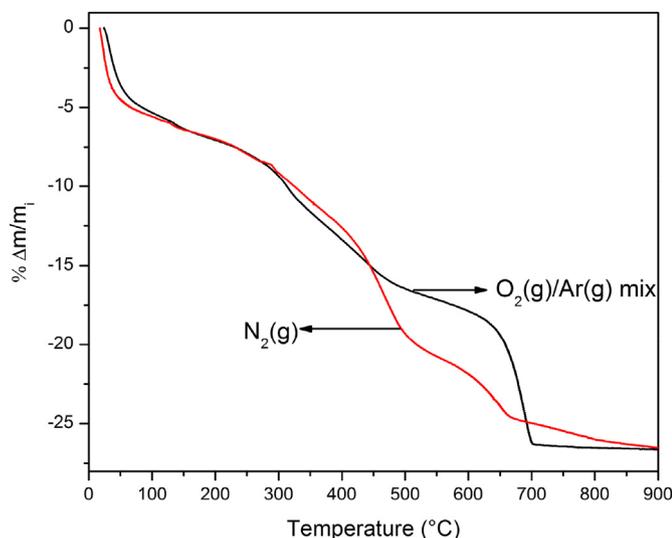


Fig. 1. Non isothermal thermogravimetries of precipitate in O₂/Ar mix and N₂.

2. Materials and methods

The gases used in the present study were: Cl₂(g) 99.8% purity (PRAXAIR, Argentina) and N₂(g) 99.99% purity (LINDE, Argentina). The solid starting reactants were: U₃O₈(s) 99.82% purity (determined by ASTM-C1267 [11]) and Ca(OH)₂ 99.9% purity (Sigma Aldrich). Initially, Calcium hydroxide solutions were prepared by dissolving Ca(OH)₂(s) in water and filtering off any precipitated calcium carbonate, and solutions of uranyl nitrate of 1.5 gU l⁻¹ by dissolving U₃O₈ in concentrated nitric acid. Then, the solutions of uranyl nitrate were treated with the Ca(OH)₂ solutions. It was observed the formation of precipitate when the pH was 4, with formation of colloid precipitates and the flocculent form changed into a granular material at pH 11. The solid products were filtrated and dried in vacuum. The uranium concentration in the supernate at pH 11 was analyzed by arsenazo-III method (pH: 1.5 and λ: 650 nm) and it was 50 mg l⁻¹ [12].

Precipitates were characterized by Scanning Electron Microscopy (FEI Nova Nano SEM 230), X-Ray Diffraction (XRD, Bruker D8 Advance) with Ni filtered and Cu_{Kα} radiation, and Multielement analysis was carried out by Wavelength Dispersive X-Ray Fluorescence Spectroscopy (WD-XRF, Bruker S8 Tiger). The XRD diagram showed that the precipitate is composed by crystal CaCO₃ and

exhibited high background intensity indicating that it contains a proportion of highly disordered materials in amorphous form. CaCO₃ presence is due to the introduction of atmospheric carbon dioxide in the solutions.

The precipitate was analyzed by thermogravimetry using a Thermo 400 system under atmospheres composed by O₂(g)/Ar(g) mix of 20/80 (to simulate air) and N₂(g).

Fig. 1 shows the relative mass change as a function of temperature. It showed a mass loss until the change reaches a value of % ΔM/M_i = -26.5 suggesting that the mass loss is due to the evaporation of water and loss of CO₂(g) in both cases. The X-Ray diagram of the solid product obtained (Fig. 2) was refined and the phases present were quantified by Rietveld method of the powder XRD data using the DIFFRACplus TOPAS 4.2 program [13]. For refinement, XRD data were collected in the 2θ ranges of 10–100° with a step size of 0.02° using a 1.5 s/step scan speed. The detailed results of the Rietveld refinements and the quantitative analysis are given in Table 1.

Table 2 shows the XRF results for the initial precipitates and the solid product obtained of its treatment in air at 900 °C using fundamental parameters method. The elements detected by the method used are those that have atomic number higher than Fluorine and the sum of their concentrations were normalized to 100%. The presence of Mg is due to the Ca(OH)₂ used has a little amount of this element as an impurity (which was observed in EDS analysis). The Mg/Ca ratio in the starting reactant is considerably lower than that showed in Table 2. This result could be indicating that Mg uranates are more feasible to be formed than Ca uranates being this behavior according to the results observed in the chlorination reactions which will be described in the next section.

The uranium contents in the initial precipitates and in the solid product obtained after treatment in air at 900 °C were 36 and 46 wt %, respectively [12].

Precipitations were carried out in nitrogen atmosphere to avoid the formation of CaCO₃ using uranyl nitrate solution and Ca(OH)₂ treated at 900 °C in air to form CaO and to eliminate CaCO₃. The XRD analyses of the precipitate did not evidence presence of carbonate and it is composed by materials in the form of amorphous. The precipitate was treated at 900 °C and the solid product obtained was analyzed by XRD which indicated the formation of CaUO₄ as single phase.

3. Thermodynamic foundations

In order to find the optimal reaction conditions for the recovery

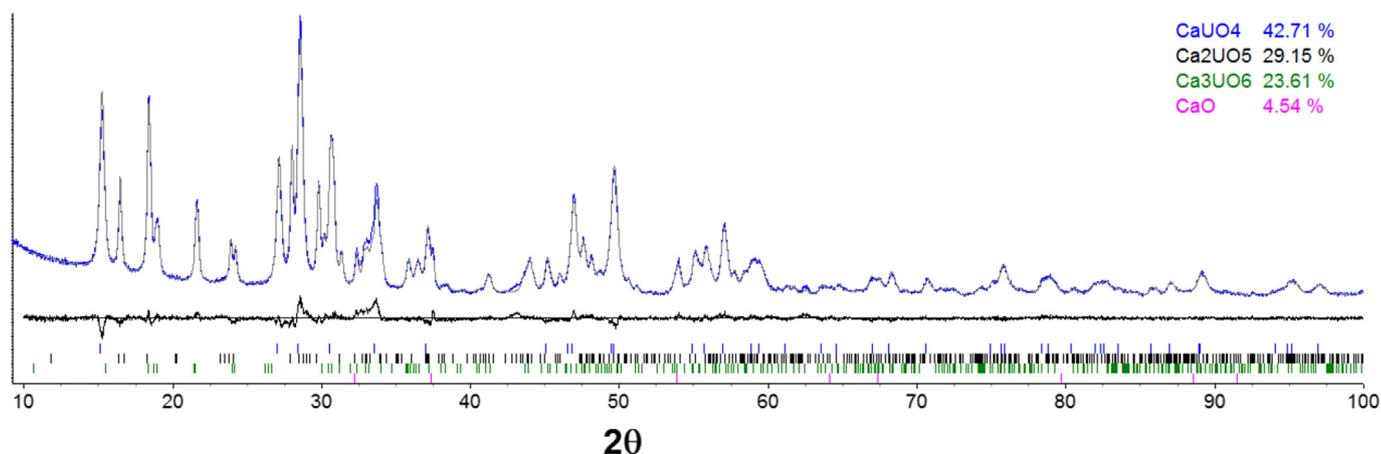


Fig. 2. Rietveld refinement of precipitate treated in O₂(g)/Ar(g) mix observed (top), and difference (bottom) profiles.

Table 1
XRD analysis of the precipitate treated in O₂/Ar mix. Rietveld refinement.

Compositions	wt. %	Space Group	Lattice parameter (Å)
CaUO ₄	42.7	R-3mR	6.267, $\alpha = 36.05$
Ca ₂ UO ₅	29.2	P121/c1	7.914, 5.438, 11.465, $\beta = 109.03^\circ$
Ca ₃ UO ₆	23.6	P1211	5.727, 5.946, 8.291, $\beta = 90.52^\circ$
CaO	4.5	Fm-3m	4.810
Rexp: 2.77 Rp: 3.89 GOF: 1.85			

Table 2
XRF analysis of the initial precipitate and solid treated in O₂/Ar mix.

Elements	wt % - initial precipitates	wt % - solid treated at 900 °C
U	59.48	59.32
Ca	32.06	30.72
Mg	4.37	5.34
Si	2.83	3.23
Al	0.59	0.67
Fe	0.58	0.60
Ti,Mn,S,Ni	<0.04	<0.04

of uranium, thermodynamic simulation of the chlorination of Ca-Mg uranates with Cl₂(g) was performed using the HSC chemistry 6.1 software for windows [14]. CaUO₄ and MgUO₄ were used as starting materials due to these are the only Ca and Mg uranates reported in this software.

Fig. 3 shows the Kellogg diagrams for the U-Cl-O, Ca-Cl-O and Mg-Cl-O systems at 400 °C and 700 °C. The axes of the diagrams are the logarithms of the partial pressure of O₂(g) and Cl₂(g). At the beginning of the chlorination reactions, the values of the partial pressure of Cl₂(g) and O₂(g) were 1 and 10⁻⁴ atm respectively, and these are indicated by a square. O₂(g) is considered as an impurity and a product of the reaction.

In the U-Cl-O system, the experimental conditions are close to the equilibrium line between UO₃ and UO₂Cl₂ at 400 °C, whereas they are on the equilibrium line between U₃O₈ and UO₂Cl₂ at 700 °C. A similar behavior is observed in the Mg-Cl-O system, where the equilibrium line between MgO and MgCl₂ is close to the experimental conditions (at 400 and 700 °C). In contrast, in the Ca-Cl-O system the formation of CaCl₂ is expected according to the calculations.

The main possible reactions which may be involved considering the reagents CaUO₄ and MgUO₄ in chlorine atmosphere are:

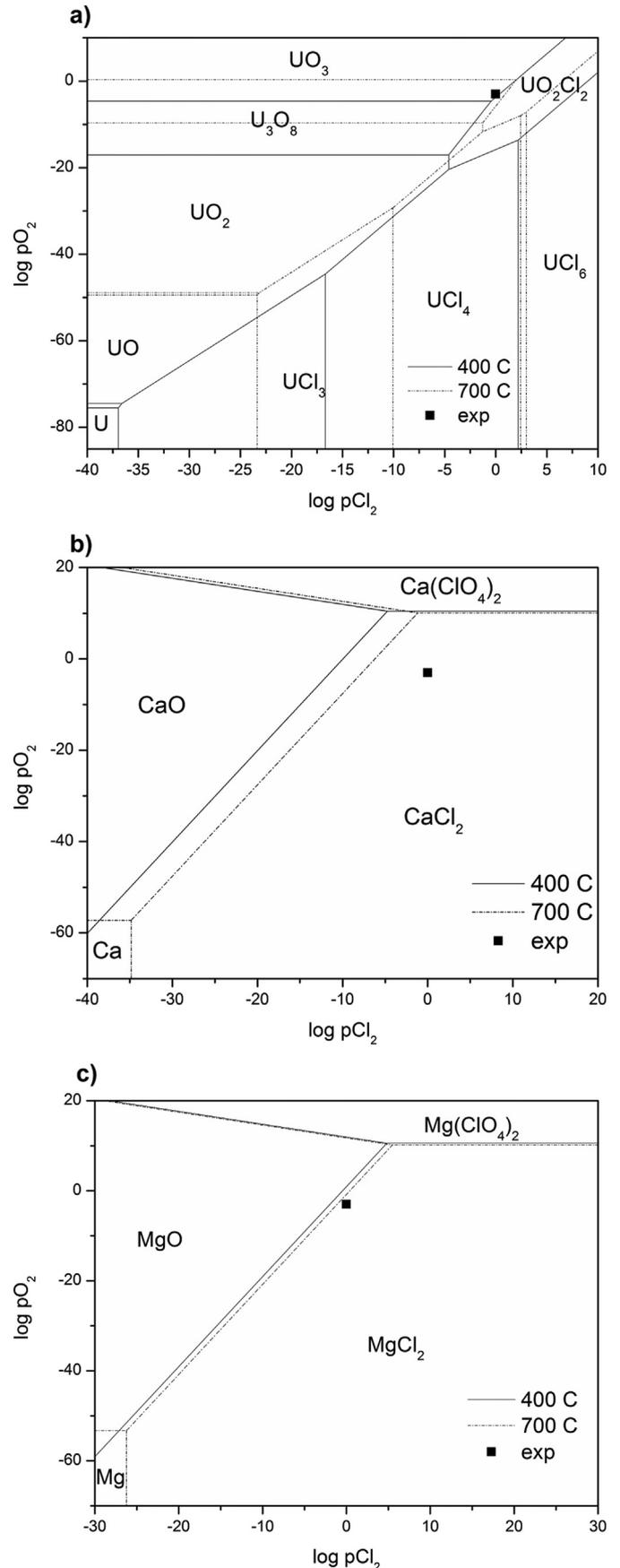
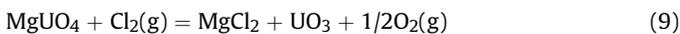
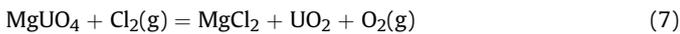
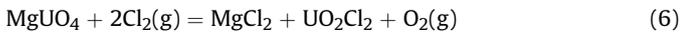
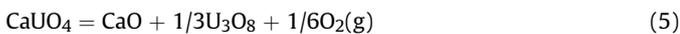
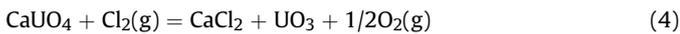
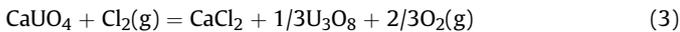
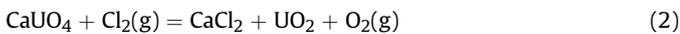
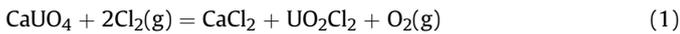


Fig. 3. Kellogg diagrams for the a) U-O-Cl, b) Ca-O-Cl and c) Mg-O-Cl systems.

Fig. 4 shows the Ellingham diagram for the reactions 1 to 10. They summarize the evolution of standard free energy changes per mol of Alkaline earth uranate, ΔG , as a function of temperature. The formation of uranium chloride compounds was not considered due to it has $\Delta G > 200$ kJ throughout the temperature range analyzed.

The chlorination reactions of calcium uranate with formation of U_3O_8 , UO_3 or UO_2 and $CaCl_2$ have the lowest ΔG of the reactions analyzed in the system $CaUO_4-Cl_2(g)$. Nevertheless, the ΔG values are positive for temperatures above 400 °C (where the chlorination experiments were performed). According to the reaction of decomposition of UO_3 (reaction 11), for temperatures above 672 °C the more stable specie will be U_3O_8 . The formation of the octooxide is expected at high temperatures [15]. Also, the UO_3 is not expected in the experiments due to the very low oxygen partial pressure in the system, for this reason the reaction 11 is displaced to the formation of U_3O_8 according to the Le' Chatelier principles.

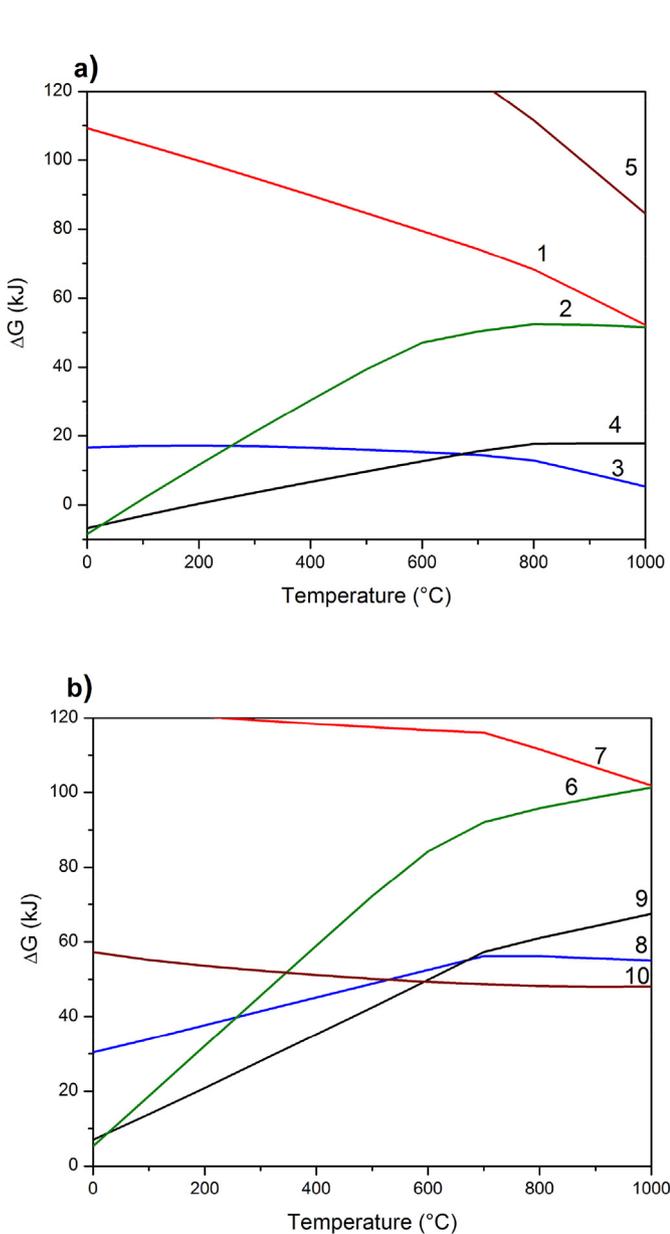


Fig. 4. Ellingham diagrams for the reactions involved in the a) $CaUO_4-Cl_2(g)$ and b) $MgUO_4-Cl_2(g)$ systems.

In the system $MgUO_4-Cl_2(g)$, the reaction with lower ΔG is that which produces UO_3 and $MgCl_2$ until 600 °C, and the $MgUO_4$ decomposition which conduces to the formation of MgO and U_3O_8 at higher temperatures. This behavior could be associated that magnesium uranate has a high stability against chlorine.

Fig. 5 shows the equilibrium composition (EC) as a function of temperature according to equilibrium predictions between 0 and 900 °C. The raw materials for the simulation were: solid phases: $CaUO_4$ (Fig. 5a) and $MgUO_4$ (Fig. 5b), and gaseous phase: 99.99% of Cl_2 (in the molar ratio of 5/1 with respect to uranate) and 0.01% of N_2 . It can be seen that UO_2Cl_2 are not expected to be formed at temperatures higher than 450 °C in both systems, but the formation of alkaline earth chlorides is predicted only in the system with $CaUO_4$ for these temperatures. The formation of U_3O_8 and UO_3 is expected in the system with Ca but they are predicted only in small amount in the system with Mg (0.5% for U_3O_8 and 4% for UO_3). Another remarkable difference between Ca and Mg systems is the

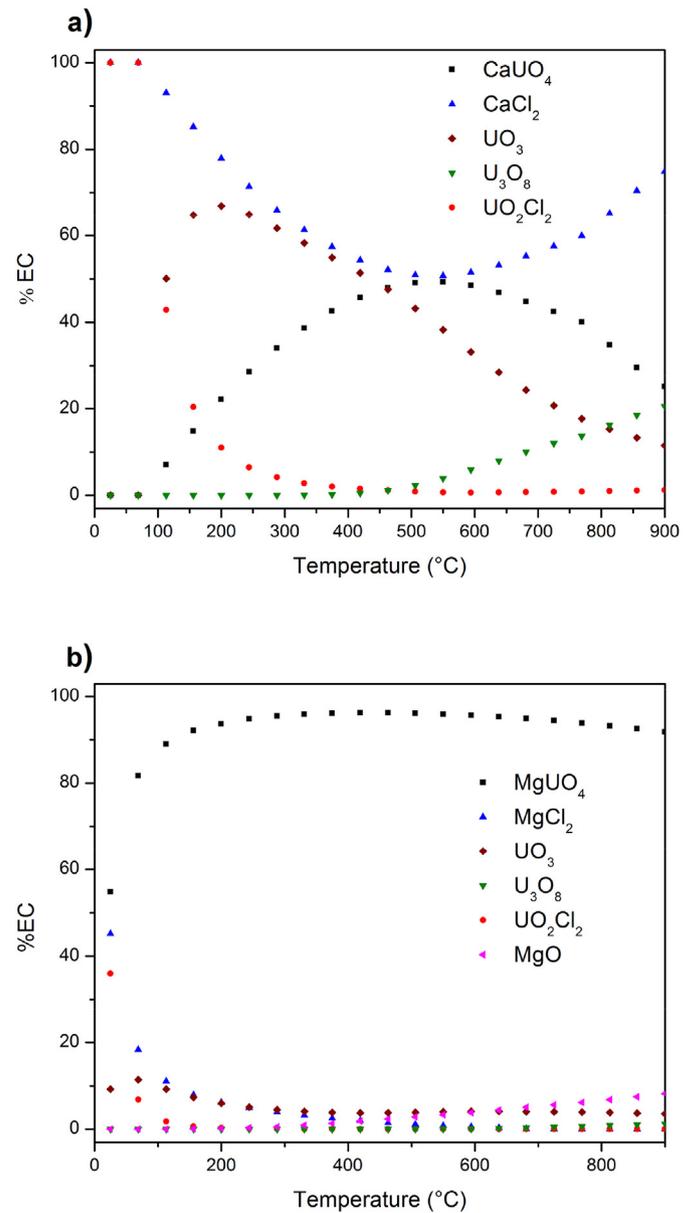


Fig. 5. Percentage equilibrium composition (%EC) as a function of temperature according to equilibrium predictions between 0 and 900 °C in the a) $CaUO_4-Cl_2(g)$ and b) $MgUO_4-Cl_2(g)$ systems.

Table 3
Chlorination reactions: mass changes and XRD analyses of the washed products (Final XRD).

Temperature (°C)	Time (h)	Mass change (wt %)	Final XRD (after washing)
300	2	−3	CaUO ₄ Ca ₂ UO ₅ Ca ₃ UO ₆ CaO (the same as initial sample)
400	8	9.3	CaUO ₄
500	2/6	8.8/18.2	CaUO ₄
600	8/12	21.0/20.4	U ₃ O ₈ Ca ₂ U ₃ O ₁₁ MgU ₃ O ₁₀ MgU ₂ O ₂ (SiO ₄) ₂ (H ₂ O) ₄
650	8	22.5	U ₃ O ₈ MgU ₃ O ₁₀ MgU ₂ O ₂ (SiO ₄) ₂ (H ₂ O) ₄
675	8	22.3	U ₃ O ₈ MgU ₃ O ₁₀
700	4	22.8	U ₃ O ₈ MgU ₃ O ₁₀
700	8	24.0	U ₃ O ₈ MgU ₃ O ₁₀
700	10	23.6	U ₃ O ₈
725	8	20.7	U ₃ O ₈ MgU ₃ O ₁₀

equilibrium amount of the uranates. The %EC of CaUO₄ is variable along the temperature range; taking a maximum value of about 50% at 550 °C. On the other hand, the %EC calculated for MgUO₄ is between 95 and 90% at temperatures higher to 100 °C. The formation of UCl₃, UCl₄, UCl₅ and UCl₆ is not expected in these systems.

4. Chlorination experiments

With the aim of Uranium recovery from Ca-Mg uranates, isothermal chlorination reactions were performed. A quartz fixed bed reactor was employed which consists of a horizontally mounted tube of 30 mm diameter located inside an electric furnace where the sample was introduced using a silica glass crucible (area = 1 cm², high = 0.5 cm). The reactant gas was introduced when the system reaches the working temperature. When each run was finished, the reactant gas was cut off and nitrogen stream was introduced to purge the reactor.

The isothermal chlorination experiments were performed at temperatures between 300 and 725 °C, with the following experimental conditions: pCl₂(g) = 1 atm; Cl₂(g) flow = 3 L h^{−1}; m₀ = 20 mg. The hygroscopic samples were opened in glove box to be weighed and characterized by XRD (reaction product XRD).

The chlorination product was washed with water, and the precipitated solids were separated. Subsequently, the solids were dried at 100 °C and analyzed by XRD (Final XRD). The difference between the reaction product XRD and the Final XRD was the presence of CaCl₂, except for the reaction at 300 °C where there was not change with the initial sample. Table 3 shows the XRD analyses and mass changes of the chlorination reactions. It was observed the formation of a single calcium uranate phase (CaUO₄) at 400 and 500 °C, indicating that Ca₂UO₅ and Ca₃UO₆ react with Cl₂(g) to form CaUO₄ and CaCl₂ at these temperatures. So, the reactions at temperatures higher than 500 °C can suppose such as the chlorination of this phase. It was observed the formation of U₃O₈ and MgU₃O₁₀ and a mass change (wt %) of about 22% at temperatures between 600 °C and 725 °C.

Fig. 6 shows the Final XRD at 700 °C and its comparison with the reference patterns U₃O₈ [16] and MgU₃O₁₀ [17,18], it can be seen

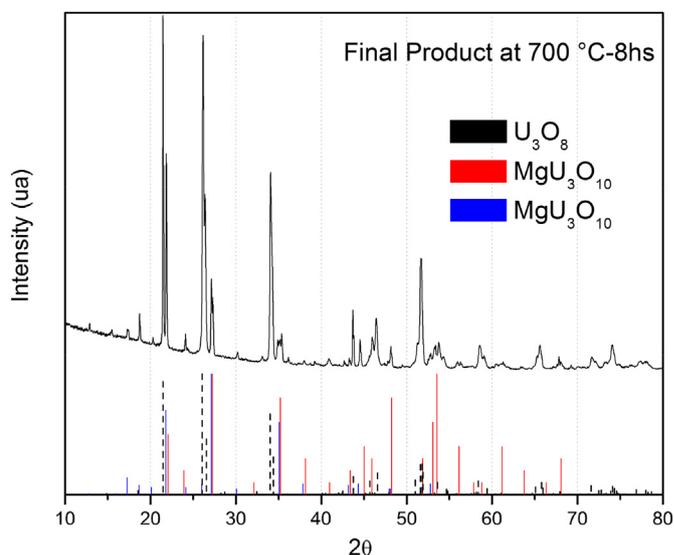


Fig. 6. Final XRD of the reaction for 8 h at 700 °C. U₃O₈ and MgU₃O₁₀ patterns.

there is a good agreement between references and experimental peaks. MgU₃O₁₀ is observed in two different phases which are showed in Fig. 6. The products were yellow or orange, except the products obtained in the reactions at 700 °C during 8 and 10 h s which were black. This condition is due to that the main product at 700 °C was U₃O₈.

Fig. 7 shows the Final XRD of the reactions for 8 h at 675, 700 and 725 °C between 25.5 and 28° of 2θ. In this figure, it is observed that the intensity of U₃O₈ peaks are maximum at 700 °C, on the other hand, the peaks of MgU₃O₁₀ are minimum at this temperature. It suggests that the temperature appropriate to formation of U₃O₈ is 700 °C, but the phase MgU₃O₁₀ is present if the reaction is carry out for 8 h. So, reaction during 10 h was done and U₃O₈ was observed in the Final XRD such as single phase (Fig. 8). Uranium oxides are extremely stable in the environment and are thus generally considered the preferred chemical form for uranium storage.

In reaction at 725 °C, it is observed a mass change (wt %) of 20.7%, being lesser than that obtained at 700 °C. Also, it is evidenced the presence of a brown yellow condensed phase in the cold

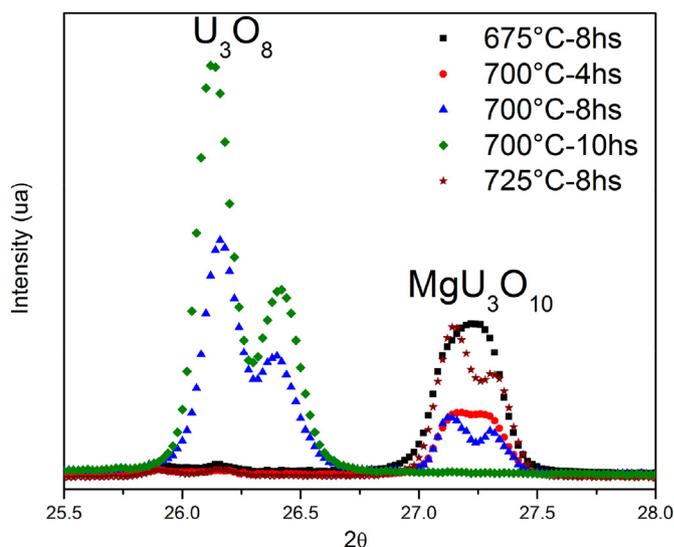


Fig. 7. Final XRD of the reactions at 675, 700 and 725 °C between 25.5° and 28° of 2θ.

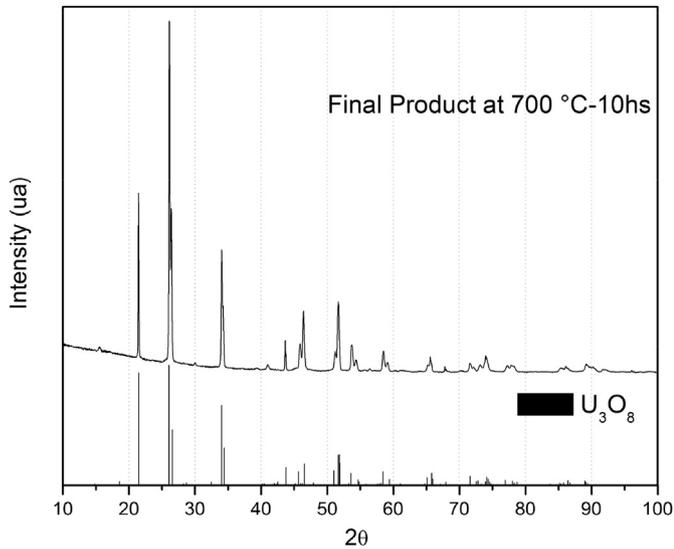


Fig. 8. Final XRD of the reaction for 10 hs at 700 °C and U_3O_8 pattern.

zone of the reactor which can be attributed to the formation of $UO_2Cl_2(g)$ during the reaction [19], being this condition not desired to uranium recuperation.

5. Energy-dispersive spectroscopy (EDS) and SEM images of Final product

EDS analyses were performed in the Final products to determine the evolution of content of main elements. The samples were mounted on carbon tape and analyzed using a 30 kV accelerating voltage and an accumulation time of 200 s. The results are shown in Fig. 9, where it can be observed the content of U, Ca, Mg and Si of Final samples for different reactions. Such as was observed in the XRD analysis, the concentration of uranium increases for the chlorinations between 500 and 700 °C and it is maximum in the reaction at 700 °C during 10 hs. The concentrations of Ca and Mg

are minimum in this condition and they have lower concentration than the quantification limit. Also, in the figure it is showed the evolution of Si in the reactions; the content of silicon in the samples is increased when the uranium is separated of Alkaline earth elements. The presence of Si is due to the sample contamination with glass and silica materials and it is not separated by chlorination method. Nevertheless, Silicon is easily separable by chlorination at high temperature [19] or by acid digestion, for example with nitric acid where the uranium oxide is highly soluble [20].

Fig. 10 shows SEM images of Final product of the chlorination at 700 °C during 10 hs. These micrographs show an average particle size between 1 and 10 μm (Fig. 10a) and two different morphologies (Fig. 10b); the rectangle-shaped particle and small size ($1 \times 3 \mu m$) was analyzed by EDS and it was determined that these particles are U_3O_8 ; by the other hand, the amorphously shaped particles are mainly composed by SiO_2 . Fig. 10b is representative of whole sample and SEM results agree with XRD results where U_3O_8 crystallized in an orthogonal system and SiO_2 is not observed because it has an amorphous structure.

6. Final remarks

In this work the chlorination of two different alkaline earth uranates were presented. It was observed that the starting temperature in the chlorination of Ca uranate and Mg uranate are different, and this behavior could understand considering the reactivity of the alkaline earth oxides with chlorine. In the bibliography, studies of CaO and MgO chlorinations were reported; in the CaO chlorination with formation of $CaCl_2$ was determined a starting temperature of reaction at around 330 °C [21] and the starting temperature for the MgO chlorination was about 700 °C [22]. These temperatures agree with the results obtained in this work where Ca uranates react at temperatures above 300 °C and Mg uranates at temperatures higher. These observations suggest that the alkaline earth uranates chlorination can be understood as the chlorination of uranium oxide and of alkaline earth oxide independently. In addition to chlorination reactions with formation of alkaline earth chloride, the possible reactions between these chlorides and U_3O_8 should be considered [18]. This can explain the

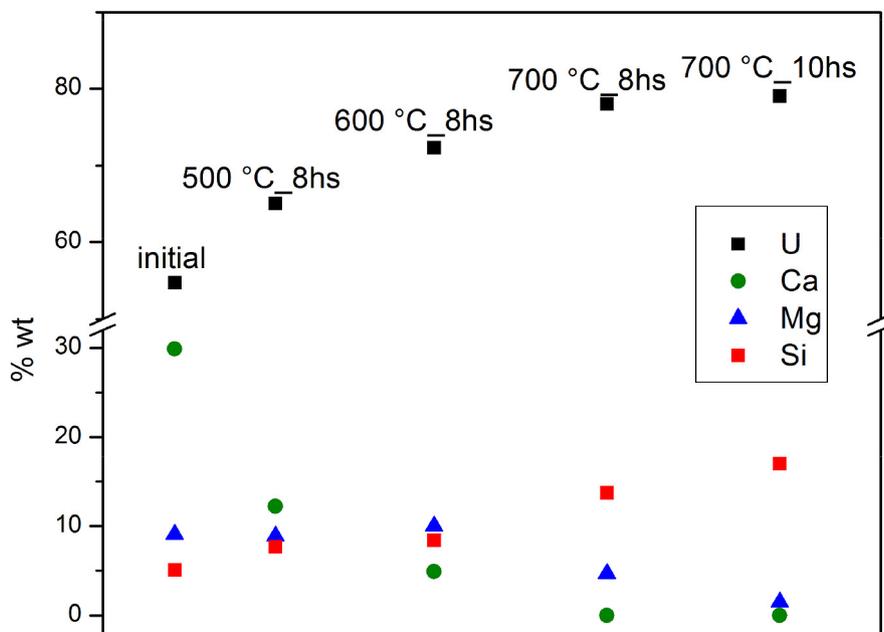


Fig. 9. EDS analyses for the Final products.

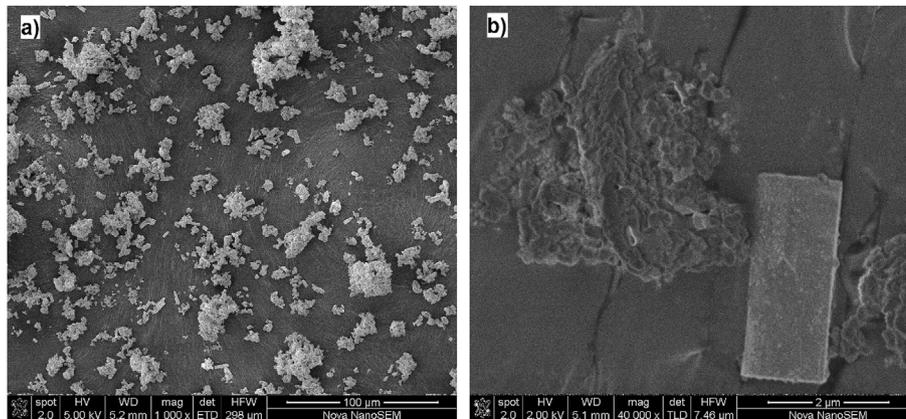


Fig. 10. SEM images of Final product of the chlorination at 700 °C during 10 hs. a) $\times 1000$ and b) $\times 40000$ magnification.

result found in the chlorination at 725 °C where it is observed the recombination between MgCl_2 and U_3O_8 .

7. Conclusions

The reaction between Ca-Mg uranates and gas chlorine was analyzed. The uranates were obtained by precipitation from uranyl nitrate solutions and calcium hydroxide. A thermodynamic study of the chlorination of CaUO_4 and MgUO_4 was performed. The results obtained in this work show that the optimal condition of uranium recuperation by chlorination of Ca-Mg uranates was 10 hs of reaction time at 700 °C using 3 l/h of $\text{Cl}_2(\text{g})$. The uranium compound obtained was U_3O_8 which is separated of other products by washing with water. Chlorination reactions performed at lower temperatures do not achieve the Mg uranate chlorination, whereas at temperatures higher than 700 °C some of the uranium is loss as volatile UO_2Cl_2 . The experimental results agree with the thermodynamic study.

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