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EVALUATION OF MICROWAVE TECHNOLOGY IN THE ADDITIONAL PURIFICATION OF Mo-99, PRODUCED FROM LEU TARGETS

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ABSTRACT

In the present work, the feasibility of the microwave technology was studied as an additional purification step (sublimation) in the production of Mo-99, via the alkaline dissolution of LEU (low enrichment uranium) targets of UAlx/Al, in the RMB (Brazilian Multipurpose Reactor) project, which is usually accomplished by induction furnace. The intention was to decrease the time spent in this purification step, for later comparison between the methods. Thus, non-radioactive samples of sodium molybdate (solution) and appropriate catalysts/materials (which could withstand up to 1300°C) were prepared and employed. All experiments were performed in a microwave oven scale (1000W/2.45GHz), under atmospheric pressure. Considering that the experiments with induction furnace lasted from 1.5h to 2h for the sublimation of oxide and molybdenum separation, the preliminary results, obtained in this study, demonstrated the time savings and the possibility of reaching temperatures up to 1200°C in less than 30 minutes. Therefore, the use of this technique is considered promising for this application, although other studies and specific devices are required.

1. INTRODUCTION

Radioisotopes play an important role in nuclear medicine and may be used in the diagnosis and therapy of several diseases, such as cancer, kidney obstruction, dementia and others. Technetium-99m (Tc-99m), the daughter isotope of molybdenum-99 (Mo-99), is the most commonly used element in this medical specialty, due to its favorable nuclear properties (half-life 6h), representing about 80% of all “in vivo” diagnostic procedures. In 2007, however, the supply of Mo-99 decreased owing to the shutdown of nuclear reactors in Canada and Belgium. Brazil had to search for other suppliers. In order to solve this problem, since 2008, Brazil has developed, in the Brazilian Multipurpose Reactor (RMB), the research and production of Mo-99 [1].

Mo-99 may be produced using UAlx targets with high uranium enrichment (HEU) and low uranium enrichment (LEU), however, in 1992, the supply of HEU targets was restricted for use in fuels and targets, forcing Mo-99 producing countries to research the use of LEU targets. In the case of targets consisting of UAlx/Al, two types of dissolution may be achieved, acid and alkaline. The latter type was adopted by Argentina and Brazil (in the RMB), with the purification of the product in chromatographic columns [2].

The production of Mo-99 with UAlx targets consists of the following phases: target irradiation; decay of short half-life products; dissolution of the targets with alkaline solution; retention of gases released at the dissolution for radioisotopes recovery; filtration for insoluble material retention; purification of Mo-99 present in the alkaline solution, after filtration by chromatographic columns; sublimation (additional purification step). After irradiation, Mo-99 is produced by U-235 fission and other radioisotopes are, also, formed (contaminants - some from early hours decay, but others with half-lives of hundreds of years and high rate of toxicity to humans). Therefore, Mo-99 purification is really relevant. Worldwide, several purification processes for Mo-99 have been reported, from UAlx targets using ion exchange columns, owing to the International Atomic Energy Agency (IAEA) resolution stating that fuels or targets could only be used with low enrichment (LEU, 20% of U-235). With the change in the type of irradiation targets, the recovery of the uranium without fission is practically unrelated to whether the target is LEU or HEU. However, it was necessary to make adaptations in the purification processes, due to the increase in the quantity of fission products and actinides, resulting from the highest proportion of U-238 [3,4,5]

In this work, the additional purification step was emphasized, using the microwaves as the heating method, to evaporate and sublimate the Mo-99 and other impurities that have remained in it.

In 2008, microwave studies in this area were described for the conversion of HEU (high uranium enrichment), uranium oxide and the pre-treatment of uranium samples for the analysis of radioactive elements. It was observed that this technique presented a great potential to improve nuclear fuel processing, with reduction of time and temperature, as well as an increase in the recovery of elements [6].

In 2011 [7], the authors reported research initiated in 1999, in which alternative technologies were already studied to obtain Mo-99 and Tc-99m separation with microwave (385W) for drying, after filtration of the precipitated solution $ZrOCl_2.8H_2O$, from the Na_2MoO_4 solution. It was found that, with the microwaves, the drying for use in a generator would be of only 35min., compared to 16 hours required by the hot air drying method [8].

At IPEN-CNEN/SP, alkaline dissolution studies have been developed to obtain Mo-99 from irradiated UAlx-Al LEU targets. In one of these works [9], in 2013, alkaline dissolution of Al6061 and Al1050 was used to simulate this process of dissolution of these types of targets. These studies were carried out because the processing time should be minimized, considering that the half-lives of Mo-99 and Tc-99m are 66h and 6h, respectively.

Therefore, before opting for any of the processes for Mo-99 production at RMB, each of them would be under studies in Brazil, and only then the final choice will be made. In addition, these Mo-99 separation and purification steps involve the use of chromatographic columns of alumina and ion-exchange resins to achieve the pharmaceutical specifications, necessary for its use in disease diagnostics.

In 2017, the final development of the prototype for alkaline dissolution of targets for Mo-99 production was reported, after 5 years of studies in the RMB project, with the implementation of a pilot unit for the production of Mo-99 and I-131, via alkaline dissolution from LEU targets of UAlx [10]. In studies of purification of Mo-99 by sublimation in a tubular furnace,

it was reported that 1mL of NH_4MoO_4 solution was sublimated in 5min, at 800°C (with more 27min, to reach this temperature), obtaining 98 ± 0.7% recovery yield of Mo-99 [11].

In this context, the objective of this work was to use the microwaves to achieve an alternative process in the additional purification stage, saving heating time and electric energy.

2. EXPERIMENTAL

Microwaves are non-ionizing electromagnetic energies, which occur at frequencies in the range of 300MHz to 300GHz (wavelength 1m to 1mm). The mechanism of microwave heating consists part of the electromagnetic energy being absorbed by the material and converted into heat (kinetic energy and potential energy of the molecules of the matter - microwaves cause molecular motion by migration of ionic species and/or rotation of dipolar species, and this raises the temperature of the material) [12, 13, 14].

The experiments were performed using a microwave oven (Panasonic - model NNS56BH - nominal power 1000W, frequency 2.45GHz), involving the following variables: sample mass (mg); temperature (°C), heating time (min.) and microwave power (W), under atmospheric pressure. The option adopted was to prepare and use samples of sodium molybdate aqueous solution $Na_2MoO_4.2H_2O$ - 241.95g/L - 1M (Shynth, purity of 99.5%-103.0%), non-radioactive, since the behavior of the compound was not known in the presence of the microwaves (supplied by the RMB group that is already conducting studies in this area, but with the conventional heating method, through induction furnace).

In order to accomplish the tests, apparatuses were set up where the samples (1g to 5g) were heated with microwaves, in sample holders of various geometries (test tube, conical flask, pointed flask, navicular, crucible and beaker) and materials (borosilicate, quartz, ceramics, mica, grafoil, soapstone), with baths using microwave absorbers (magnetite, CoMo-based catalyst, graphite powder, charcoal and silica - individually or in combination). The heating time varied up to 10min and the samples temperatures were measured (k type thermocouple/Salvterm 1200K) under atmospheric pressure.

3. RESULTS

Initially, essays were accomplished without immersion of sample-holders in bath and the samples evaporation was observed in 3min., even using a glass sample-holder (beaker).

However, in addition to the increase of the heating time, the intended temperature (about 1200°C) for the start of sublimation was not reached. Then, another trick was tried to solve this problem, placing the sample holders in baths, with materials that could be good absorbers of microwaves.

Thus, several materials were tested in order to find that which could better transmit/absorb microwave radiation for the sample (in heat form) or be transparent to the microwaves, besides withstanding high temperatures (up to 1300°C). When the bath materials were heated separately, they did not perform well, reaching only 120°C.

However, when combined, the results obtained were much better. The bath that gave the best performance was the combination of magnetite and CoMo-based catalyst. The highest temperature found for this bath was 1200°C, in a heating time of 6min.

From all the materials tested for sample-holders, soapstone and ceramics (despite being transparent to microwaves) were the ones that presented the worst performance as absorbers and heat conductors for the sample. The best option was quartz, which provided higher temperatures, without any damage. These results corroborate the technical data on quartz, which stands temperatures up to, approximately 1700°C.

The geometry of sample-holders that provided the highest temperatures and without any damage was the conical flask and the pointed flask, both of quartz. In several assays, hot spot in the samples was reached and, in the best test occurred within 16min. heating, with the sample at 1065°C, in a quartz sample holder (pointed bottle), magnetite bath and CoMo-based catalyst. This demonstrated the large heating capacity of the bath composition, sample-holder geometry and the material. In the Fig. 1, the apparatus set is visualized, making the hot spot in the sample-holder evident. It is worth mentioning that this type of experimental arrangement was well reproduced in other tests and it could be applied safely and reliably to heat samples.

Figure 1: View of the test apparatus, showing the hot spot in the sample-holder.

Damasceno, in 2019 [15], cited the evaporation and drying of a solution of NH_4OH, containing $(NH_4)\ 2Mo_4$ (in a platinum crucible), in temperature below 100°C, using a heating plate, but the time was not cited. Then, this crucible with the dried sample was placed in a conventional tubular furnace and heated up to 850°C (sublimation temperature) under the following conditions: heating rate 15ºC/min. (about 55min.), heating time after reaching the sublimation temperature (plateau) – about 20min. Therefore, the total time was 75min, without considering the time for the sample to reach 100ºC.

4. CONCLUSIONS

Taking into account that induction furnace experiments (for the RMB design) last from 1.50min. to 2h for the sublimation of oxide and molybdenum separation, the preliminary results obtained in this study demonstrated the time savings and the possibility of reaching temperatures in the samples up to 1065°C and, in the bath, up to 1200°C. From the results obtained so far, the use of this technique is considered promising for this application, but it requires further studies and it needs to be improved, with specific devices for the continuity of the tests. For this optimization in the process of molybdenum purification and its subsequent separation, it was observed that it is necessary to develop and make a more suitable sample-holder in quartz, including the design, manufacture and assembly of an automated system with microwaves (with the possibility of variation of power) and peripherals, such as flow controller, phase separator, heat exchanger, on-line temperature measurements, among others. Thus, for this stage of the element separation process, it will be possible to reduce the time, with consequent reduction of capital and operating costs.

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