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DISSOLUTION OF TARGETS FOR THE PRODUCTION OF MO-99: PART 1. INFLUENCE OF NAOH CONCENTRATION AND THE ADDITION OF $NaNO_3$ AND $NaNO_2$ ON THE DISSOLUTION TIME

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ABSTRACT

Faced with global crisis in the production of radioisotope ^{99}Mo, which product of decay, ^{99m}Tc, is the tracer element most often used in nuclear medicine and accounts for about 80% of all diagnostic procedures *in vivo*, since September 2008 Brazil is developing the project called Brazilian Multipurpose Reactor (RMB). Within the Brazilian Nuclear Program (PNB) the construction of the RMB, is seen as a long term solution to meet all domestic demand relative to the supply of radioisotopes and radiopharmaceuticals. In the process to be studied to obtain ^{99}Mo from irradiated UAl_x-Al LEU targets employing alkaline dissolution, processing time should be minimized, considering the short half life of ^{99}Mo and ^{99m}Tc, about 66 h and 6 h, respectively. That makes dissolution time a significant factor in the development of the process. This paper presents the results of alkaline dissolution of "scraps" of Al, used to simulate the dissolution process of UAl_x-Al targets. Al corresponds to about 79% of the total weight of the UAl_x-Al target. The effect of NaOH concentration on dissolution time for the interval of 1 to 3.5 $mol.L^{-1}$ was studied, keeping the molar ratio in 1Al:2.16NaOH and the initial temperature of 88°C. The influence of reagent composition over dissolution time was studied using three different solutions: a) 3 $mol.L^{-1}$ NaOH, b) 3 $mol.L^{-1}$ $NaOH/NaNO_3$ and c) 3 $mol.L^{-1}$ $NaOH/NaNO_2$, keeping the same molar ratio and temperature. The results showed that the dissolution time decreases with increasing NaOH concentration and the addition of $NaNO_3$ or $NaNO_2$ in the NaOH solution reduces both dissolution time and volume of gases released.

1. INTRODUCTION

Radioisotopes play an important role among the peaceful uses of nuclear energy. Radionuclides in nuclear medicine can be used for diagnosis and therapy. ^{99m}Tc from ^{99}Mo is the tracer element most commonly used in nuclear medicine because of its favorable nuclear properties, accounting for about 80% of all diagnostic procedures *in vivo*. Currently, the supply of this important radioisotope is deficient due to the shutdown of the reactors in Canada and Belgium, the world's largest producers. So Brazil had to seek other suppliers, such as Argentina and South Africa to meet their needs, even partially.

In order to solve this problem of dependence on the producing countries, Brazil develops now the project named Brazilian Multipurpose Reactor (BMR), which began on September 2008, for research in nuclear area and for the production of ^{99}Mo, estimated in 1,000 Ci/week.

Within this project we intend to study two lines of research to obtain ^{99}Mo from the fission of ^{235}U. The two surveys cover different types of targets with low enrichment (< 20% of ^{235}U). The first studie will be with targets of UAl_x-Al via alkaline dissolution and the second with metallic uranium foils via acid dissolution.

The Nuclear Fuel Center (NFC) at Nuclear and Energy Research Institute (IPEN-CNEN/SP) dominates the manufacturing technology of UAl_x-Al miniplates, for this reason the studies preferably started with this type of target. So far there is no country that produces ^{99}Mo from metallic uranium targets commercially. Among the countries that are studying the fabrication of this type of target, South Korea and more recently USA have the knowledge of this manufacturing technique and may likely be distributors for other users.

2. GENERAL

The alkaline dissolution is a established process used by some countries that produces ^{99}Mo, for example Argentina. At the alkaline dissolution of targets UAl_x-Al [1], aluminum, some fission products and ^{99}Mo are soluble in this medium, while the uranium remains in the form of a precipitate, thus providing a first separation step [1].

This work is part of the research for the alkaline dissolution of UAl_x-Al targets. The studies were conducted with scraps of Al, the same used in the fabrication of the targets. Al represents about 79% of the total mass of the UAl_x-Al targets.

The processing time should be as small as possible, considering that the half life of ^{99}Mo is 66 h and the half life of ^{99m}Tc is about 6 h. This makes the parameter dissolution time a significant factor in the development of the process.

The dissolution of the Al scraps in an alkaline medium may have different reaction products depending on the reagent used and other factors, such as temperature, concentration, molar ratio, etc. The equations [2] involved in the process of dissolution can be seen below:

$$Al + NaOH + H_2O \rightarrow NaAlO_2 + 1.5H_2 \quad (1)$$

$$Al + 0.5NaOH + 0.5NaNO_2 + 0.5H_2O \rightarrow NaAlO_2 + 0.5NH_3 \quad (2)$$

$$Al + 0.625NaOH + 0.375NaNO_3 + 0.25H_2O \rightarrow NaAlO_2 + 0.375NH_3 \quad (3)$$

$$Al + NaOH + 1.5NaNO_3 \rightarrow NaAlO_2 + 0.5H_2O + 1.5NaNO_2 \quad (4)$$

$$Al + 0.85NaOH + 1.05NaNO_3 \rightarrow NaAlO_2 + 0.9NaNO_2 + 0.15NH_3 + 0.2H_2O \quad (5)$$

During the process of dissolution, according to equation (1), the release of hydrogen can cause problems with respect to explosion and fire, which together with the radioactive gases released may increase the radioactive risk of gas storage system.

The release of hydrogen can be minimized with the addition of $NaNO_3$ or $NaNO_2$. The amount of $NaNO_2$ and NH_3 as reaction products depends on the amount of $NaNO_3$ in the reagent [3], as it can be seen in reactions 3-5.

3. EXPERIMENTAL

3.1. Materials and Reagents

- ✓ scraps of Al;
- ✓ NaOH p.a.;
- ✓ $NaNO_3$ p.a.;
- ✓ $NaNO_2$ p.a.;
- ✓ 2L 3-neck borosilicate glass flask;
- ✓ jacketed borosilicate glass condenser with coil;
- ✓ thermostatic bath;
- ✓ water bath;
- ✓ thermocouple.

3.2. Dissolution of Aluminum

To simulate UAl_x-Al targets, hot dissolution studies (88°C) [3,4] with Al scraps were carried out. The dissolution time was chosen to evaluate the results, since it is an important parameter in the process development as a whole. Initially the influence of the concentration of NaOH in the range 1 to 3 $mol.L^{-1}$ while remaining fixed the molar ratio 1Al:2.16NaOH was studied [4]. Then the influence of the concentration NaOH in the range of 3 to 3.5 $mol.L^{-1}$ keeping the same molar ratio was studied. Finally the behavior of dissolution with different alkaline solutions: a) 3 $mol.L^{-1}$ NaOH, keeping the molar ratio in 1Al:2.16NaOH; b) 3 $mol.L^{-1}$ $NaOH/NaNO_3$, keeping the molar ratio in $1Al:2.16NaOH:2.16NaNO_3$ and c) 3 $mol.L^{-1}$ $NaOH/NaNO_2$, keeping the molar ratio in $1Al:2.16NaOH:2.16NaNO_2$ were studied. The experiments were performed in triplicate to confirm reproducibility.

4. RESULTS AND DISCUSSION

The results of the studies on the variation of the NaOH concentration from 1 to 3 $mol.L^{-1}$ can be seen in Fig. 1. It was observed that at the range studied there was a reduction of approximately 65% in the time of dissolution with increasing concentration of NaOH.

In Fig. 2 the result of the study on the variation of the NaOH concentration in the range 3 to 3.5 $mol.L^{-1}$ can be seen. The results indicated that the increase of the concentration of NaOH barely altered the dissolution time.

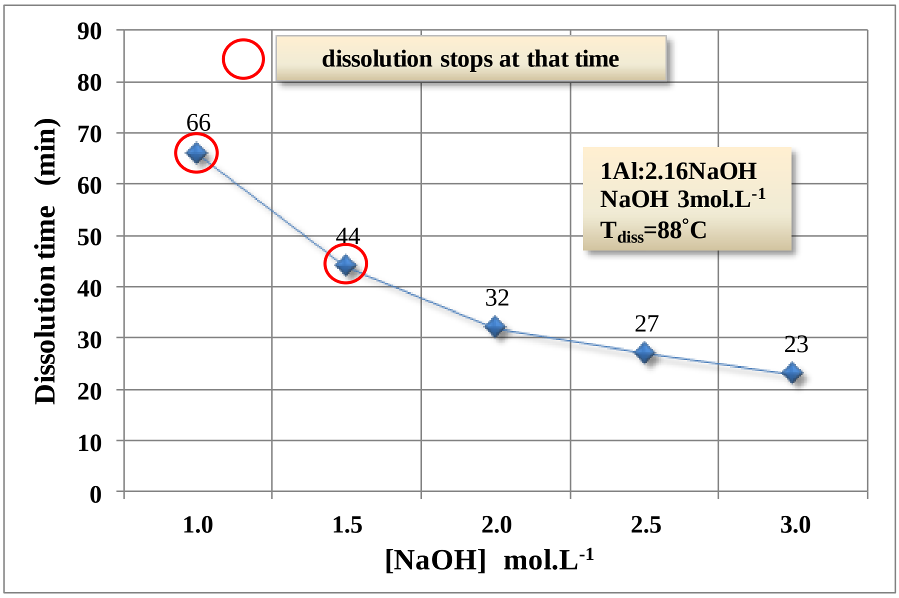

Figure 1. Influence of increasing concentration of NaOH in the time of dissolution for the range of 1 to 3 mol.L^{-1} and a molar ratio of 1Al:2.16NaOH.

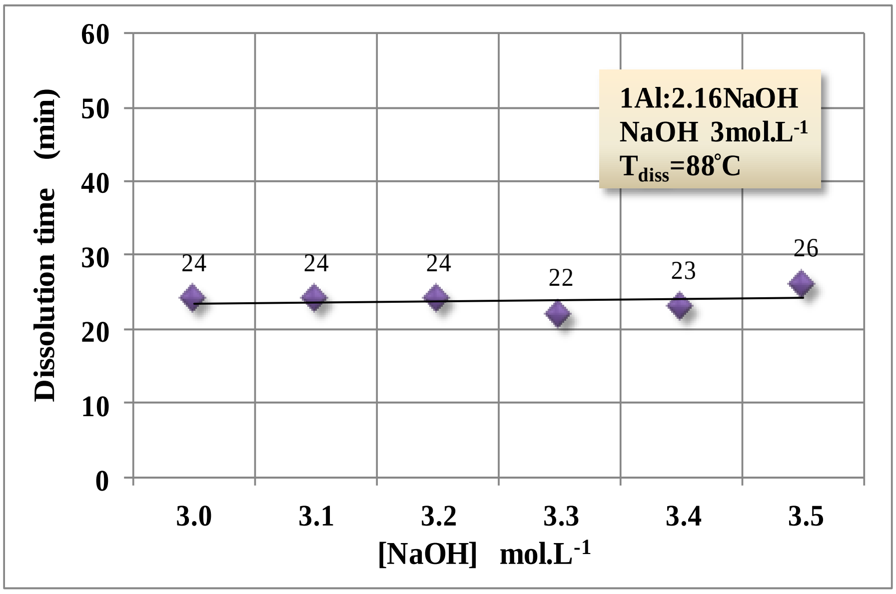

Figure 2. Influence of increasing concentration of NaOH in the dissolution time for the range 3 to 3.5 mol.L^{-1} and a molar ratio of 1Al:2.16NaOH.

In order to minimize the risk involved in storing radioactive waste, the behavior of dissolution with alkaline solutions containing $NaNO_3$ and $NaNO_2$ was studied, that according to the literature reduces the volume of gases released during the dissolution. The dissolution of Al with 3 mol.L^{-1} $NaOH/NaNO_3$ solutions and 3 mol.L^{-1} $NaOH/NaNO_2$ keeping the initial temperature of dissolution in 88°C and the molar ratios of 1Al:2,16NaOH:2.16 $NaNO_3$ and 1Al:2.16NaOH:2.16$NaNO_2$ was evaluated. The results obtained with alkaline solutions: 3 mol.L^{-1} NaOH, 3 mol.L^{-1} $NaOH/NaNO_3$ and 3 mol.L^{-1} $NaOH/NaNO_2$ are shown in Fig. 3. It was observed that there was a significant reduction of 39.13% in the time of dissolution with 3 mol.L^{-1} $NaOH/NaNO_3$ solution and 52.17% with 3 mol.L^{-1} $NaOH/NaNO_2$ solution. In relation to the volume of gases released during the dissolution, there was a very remarkable reduction of 78.99% with 3 mol.L^{-1} $NaOH/NaNO_3$ solution and 69.61% with 3 mol.L^{-1} $NaOH/NaNO_2$ solution.

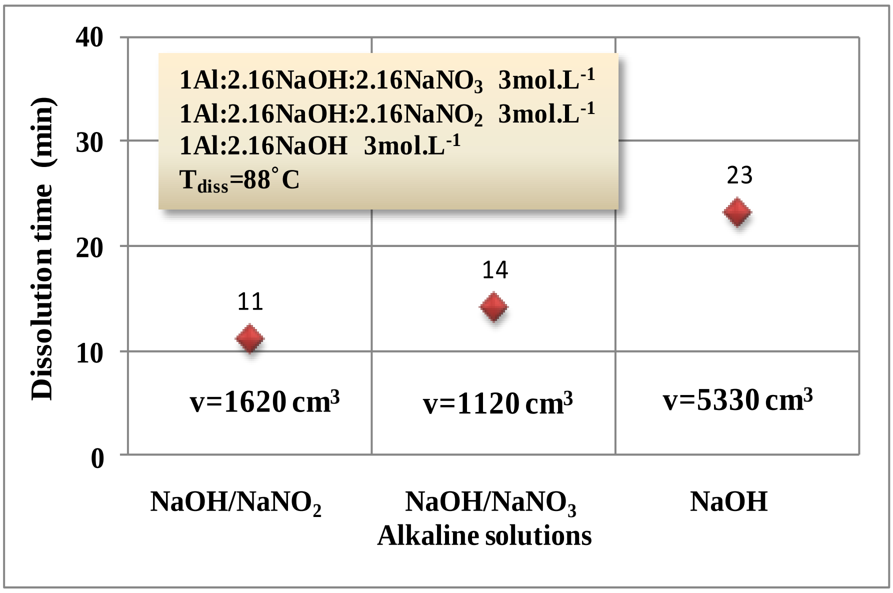

Figure 3. Influence of the alkaline solution in the time of dissolution to 3 mol.L^{-1} NaOH, 3 mol.L^{-1} $NaOH/NaNO_3$ and 3 mol.L^{-1} $NaOH/NaNO_2$ with molar ratios of 1Al:2.16NaOH, 1Al:2.16NaOH:2.16$NaNO_3$ and 1Al:2.16NaOH:2.16$NaNO_2$.

5. CONCLUSIONS

The increasing concentration of NaOH up to 3 mol.L^{-1} favored the reduction of the time of dissolution, which is considered an important factor in the choice of process variables. It was found that the addition of $NaNO_3$ or $NaNO_2$ to the solution of NaOH led to a reduction in the time of dissolution and especially a sharp drop in the volume of gas released. It was not possible to identify and quantify in % (v/v) the composition of gases released during the experiments (e.g. NH_3 or H_2), however there was a characteristic odor of NH_3 in all experiments.

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