ORIGINAL ARTICLE

Rapid simultaneous recovery and purification of calcium and molybdenum from calcium molybdate-based crystal waste

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Abstract

Molybdenum (Mo) has wide applications like as alloying elements in steel industries and in experimental laboratories as a catalyst for organic synthesis and as scintillating crystals in high-energy physics experiments. The primary mineral resources of Mo have been ceaselessly exploited and are insufficient to meet the demand in manufacturing industries and experimental researches. Separation, purification, recovery and reuse of Mo will, therefore, be of great importance for environmental conservation and sustainable development. The objective of this study was to recover Mo and calcium (Ca) from crystal wastes. Mo and Ca were recovered from $CaMoO_4$ scintillating crystal wastes in the forms of MoO_3 and $CaCO_3$ by adopting nitric acid and hydrochloric acid leaching schemes. About 98% recovery yield efficiency for both elements was obtained through hydrochloric acid leaching. The concentrations of impurity elements like strontium, barium, lead, thorium and uranium in the final products were also reduced by several dozen times as compared to the initial wastes. The finding of this study showed that the hydrochloric acid leaching method could be applied for a rapid and efficient recovery of Mo and Ca from $CaMoO_4$ wastes on a large scale.

Keywords Calcium molybdate · Crystal waste · Hydrochloric acid leaching · Purification · Recovery

Introduction

Experimental discovery of neutrino oscillation has provided conclusive evidence about the existence of non-zero neutrino masses [1]. However, we still do not know the property of neutrinos, whether they are Dirac or Majorana particles, and their absolute masses. The nature of neutrino and its absolute mass scale can be determined from the neutrino-less double beta ($0\nu\beta\beta$) decay experiments [2]. The $0\nu\beta\beta$ decay can be detected using scintillating crystal detectors containing candidate isotopes for $0\nu\beta\beta$ decay. Among the few known candidate isotopes, ^{100}Mo is comparatively the more preferred one because of its high Q value of the decay (3.035 MeV), relatively large natural abundance (9.2%) and viability for enrichment [3, 4]. Therefore, several experiments are searching the $0\nu\beta\beta$ decay from ^{100}Mo isotope [5, 6].

The Advanced Molybdenum-based Rare process Experiment (AMoRE) is searching for $0\nu\beta\beta$ decays of ^{100}Mo from molybdenum-based scintillating crystal detectors [7–9]. The AMoRE collaboration will run the experiments in a series of phases with ^{100}Mo-based scintillating crystals. The ^{48dep}Ca^{100}MoO$_4$ crystal has fulfilled most of the required properties for the AMoRE experiment compared to the previous Mo-based scintillating crystals reported [10–15]. Thus, the first phase (AMoRE-I) experiment with the ^{48dep}Ca^{100}MoO$_4$ crystals using a cryogenic technique is run at the YangYang underground laboratory (Y2L) in Korea.

A huge amount of crystal wastes in the form of the impurities concentrated at the bottom parts during crystal growth and the leftovers of crystals during shaping and sizing crystal detectors [8, 16] is produced. Discarding and

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disposing of the crystal wastes are not wise, as they contain expensive ^{48dep}Ca and ^{100}Mo. The isotopically purified and economically expensive ^{48dep}Ca and ^{100}Mo present in the crystal wastes need to be recovered and reused. Therefore, understanding the mechanism of retrieval and development of a potential technique to recover Ca and Mo from the crystal wastes is important.

Various experiments for separation, purification and recovery of Mo from leach solutions have already been performed adopting ion-exchange and solvent extraction methods [17–24]. However, large-scale separation, recovery and purification of calcium (Ca) and molybdenum (Mo) are limited due to the selectivity efficiency and distribution ratio of the methods applied. Among the various methods applied to recover Mo and Ca, the precipitation method offers a relatively simple, rapid and cost-effective alternative. Therefore, the objective of this research work was to develop an efficient precipitation technique to recover Mo and Ca from the calcium molybdate crystal wastes and to investigate the concentration of impurity. Findings of the present study could be useful for recovering Ca and Mo in a cost-effective way as well as reducing the cost of waste disposal and environmental hazards. In addition, reducing, recycling and reuse of wastes are pertinent to environment conservation and sustainable development.

Experimental

Materials and reagents

The following chemicals were obtained for the present study: nitric acid (HNO$_3$, 65%) and hydrochloric acid (HCl) (Eco-Tec Inc., Pickering, ON, Canada); ammonium hydroxide (NH$_4$OH); ammonium carbonate ((NH$_4$)$_2$CO$_3$) (Sigma-Aldrich, St. Louis, MO, USA). Calcium chloride (CaCl$_2$), ammonium nitrate (NH$_4$NO$_3$) and ammonium chloride (NH$_4$Cl) were prepared in the experimental laboratory. Single-phase crystal waste of calcium molybdate (CM) was obtained from the crystal growing laboratory of the AMoRE collaboration. The crystal waste consisted of the remains of CM melts and leftovers obtained during crystal growing and processing, respectively.

Laboratory condition

This study was conducted in a Class 1000 Cleanroom to minimize cross-contamination of radioactive elements during the experiments. All the apparatuses were made of quartz or polypropylene.

Recovery schemes

The single-phase CM crystal waste, obtained from the crystal growing laboratory of the AMoRE collaboration, was crushed into fine powder using a mortar and pestle and sieved using a strainer (Kunststoff Ø 200 mm DIN 4197, Analysensieb, Germany). One hundred grams of CM powder, in each experiment, was used to recover Mo and Ca by adopting HNO$_3$ and HCl leaching schemes. The recovery yield efficiency (RYE) in both schemes was calculated using the amount of Mo and Ca present in the initial CM and final MoO$_3$ and calcium carbonate powders.

Nitric acid leaching scheme

The CM powder was leached with two-time diluted HNO$_3$ in a portion-wise acid addition basis with continuous stirring and heating in a water bath (90 °C) for 6 h. In order for the complete leaching of CM powder to occur, 30% more acid than the stoichiometric mole ratio was used. After 6 h, when the white CM powder changed to yellowish molybdic acid, calcium nitrate solution and molybdic acid were separated using a filter paper (F1005 grade, 70 mm diameter). The molybdic acid was washed three times with 10% HNO$_3$ and dissolved in 12.5% NH$_4$OH to make the ammonium molybdate [(NH$_4$)$_2$MoO$_4$ or AM] solution. The pH of AM solution was adjusted to 8 and maintained constant for a few hours until the precipitation of CM was obtained. The precipitated CM was separated from the AM solution using filter paper (F1005 grade, 70 mm diameter). After separation of the CM from the solution, pH of AM solution was adjusted to 1.8 using HNO$_3$ to make crystalline polyammonium molybdates (PAM). The PAM precipitate was washed with 10% NH$_4$NO$_3$ solution (pH 1.8), dried and then converted into MoO$_3$ by annealing at 675 °C in air flow condition.

The calcium nitrate solution, after separation of molybdic acid, was heated (50 °C) to evaporate the excessive acid and pH was adjusted to 8 using ammonium hydroxide. The remaining calcium molybdate present in the calcium nitrate solution was separated by precipitation as in the AM solution. Ammonium carbonate powder was added to the calcium nitrate solution to obtain CaCO$_3$ as the final product. The CaCO$_3$ was filtered, washed with deionized water and dried in a vacuum oven (100 °C) until complete drying.

Hydrochloric acid leaching scheme

In this scheme, recovery experiments were conducted under two conditions: dissolution of CM powder with excessive (12−55%) HCl instead of the theoretical requirement and

different aging times (5−350 min) of polyammonium molybdate (PAM).

The CM powder was mixed with HCl (30%) according to the stoichiometric mole ratio. The mixture of CM powder and HCl was heated (70 °C) with continuous stirring until it was converted to a yellowish transparent solution. The solution was filtered through a membrane filter (0.25 μm) and the filtrate was diluted with deionized water until the concentration of Mo reached slightly less than 60 g/L. NH_4OH was added to the solution with continuous stirring using magnetic stirrer until pH 1.8 ± 0.2, when a white colored PAM started precipitating in the mixture. The PAM was aged for different time intervals, filtered through a filter paper (F1005 grade, 70 mm diameter) and washed several times with NH_4Cl buffer (pH 2).

The isolated PAM was dissolved with NH_4OH (25%) until pH 8 to make the AM solution. Few grams of CM were precipitated out from $(NH_4)_2MoO_4$ at pH 8. The CM obtained as precipitate was filtered through a membrane filter (0.25 μm pore size) and collected to calculate RYE. Further, the AM solution was crystallized by complete evaporation of excess water, dried at room temperature and weighed. The powder was annealed at 675 °C in air flow condition to convert into molybdenum oxide powder.

The solution that remained after PAM separation was $CaCl_2$ containing a little amount of unseparated Mo ions. Separation of the Mo ions from the $CaCl_2$ was conducted by adjusting pH 8 with NH_4OH. Few grams of CM powder were precipitated. The precipitates were filtered and collected as described in the HNO_3 leaching scheme. Finally, calcium carbonate ($CaCO_3$) was synthesized by reacting $CaCl_2$ and ammonium carbonate ($(NH_4)_2CO_3$). The synthesized $CaCO_3$ was dried in a vacuum oven at 100 °C until constant weight.

X-ray powder diffraction (XRD) phase analysis of $CaCO_3$ and molybdenum oxides was performed to confirm the characteristic phases of the powders synthesized in both schemes. The concentration of radioactive impurities was measured using inductively coupled plasma mass spectrometry (ICP-MS) (7900, Agilent Technologies, CA, USA) of initial and final products.

Characterization

The crystalline phase of synthesized powder was identified using XRD phase analysis (Philips XPERT-MEDX-ray diffractometer) using a CuKα source as described by Kniess et al. [25] with some modifications. The analysis was carried out in a range from 10 to 60 degree with a scan speed of 3 s per step and a step size of 0.02 A. The X-ray phases of synthesized powder were compared with that of the reference phase of a standard data available.

The ICP-MS (7900, Agilent Technologies, CA, USA) operating in collision mode was used to determine the content of impurities. The concentrations of elements barium (Ba), strontium (Sr), thorium (Th), lead (Pb) and uranium (U) were measured with the standard addition calibration method.

Results and discussion

CM is slightly soluble in cold water and maximum solubility occurs at 80 °C that refers to 0.022% [26]. NH_4OH leaching of CM is also reported well. However, after 1 h of exposure with 1% NH_4OH solution, 1.9% of the initial amount of Mo goes to the solution [21]. Hence, water or alkali leaching does not allow to get the required solubility and extraction of Mo from the solution. To respond to the high Mo extraction and recovery, acidic leaching is preferable and widely used in hydrometallurgical practices [20, 23, 24]. In case of CM, concentrated nitric or HCl might be useful, whereas sulfuric acid forms insoluble calcium sulfate ($CaSO_4$) precipitating simultaneously with molybdic acid which makes the separation process difficult.

Nitric acid leaching scheme

The CM powder was mixed with diluted HNO_3 in a portion-wise basis with stirring and heating. The equation of the reaction is given below.

$$CaMoO_4 + 2HNO_3 \rightarrow H_2MoO_4 \downarrow + Ca(NO_3)_2. \tag{1}$$
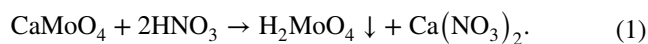
A mixture of insoluble, thick and sticky molybdic acid and $Ca(NO_3)_2$ solution was formed after 6 h of reaction. The sticky molybdic acid was very difficult to separate from the mother solution [$Ca(NO_3)_2$] through filtration. Therefore, a main loss of the Mo was expected during filtration. However, the advantage of filtration is that most of the acid soluble metal impurities can be separated from the Mo matrix. Complete separation of Ca and Mo cannot be achieved in a single step. Therefore, the molybdic acid was further dissolved in 12.5% NH_4OH solution and the pH of the solution was adjusted to 8 to precipitate out the remaining Ca ions in the form of CM present in the molybdic acid. The precipitated CM could co-precipitate few impurities like Ba, Sr, Th and U [27] and is advantageous from a purification point of view. After separation of the remaining CM, the pH of the AM solution was adjusted to 1.8 to precipitate PAM as in the following chemical equation for the final product.

$$4(NH_4)_2MoO_4 + 6HNO_3 \rightarrow (NH_4)_2Mo_4O_{13} \downarrow \\ + 6NH_4NO_3 + 3H_2O. \tag{2}$$
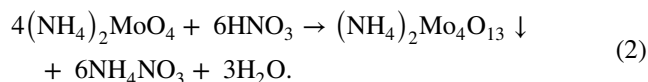
Mo ions present in the calcium nitrate solution were separated by precipitation of CM which can also co-precipitate with few impurities like Fe and other divalent metals. The complete precipitation of $CaCO_3$ can be achieved as shown in the following equation.

$$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + 2NH_4NO_3. \quad (3)$$
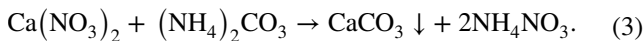
The total recovery efficiency of Mo obtained in the HNO_3 leaching scheme was 89%, out of which 74.1% was attributed to the final product and 14.9% remained in CM. In the case of Ca, 85.8% was recovered as final calcium carbonate and 16.5% remained in CM.

The HNO_3 leaching scheme may look simple and rapid to separate Mo matrix from the decomposed calcium molybdate within a few steps, however, filtering out the sticky molybdic acid from the calcium nitrate solution with subsequent washing of filter cake takes quite a long time as well as irretrievable loss of Mo also occurred. Moreover, the molybdic acid is slightly soluble in HNO_3 which makes it quite difficult to recover more than 90% of Mo.

Low Mo recovery efficiency, longer experiment time and a high requirement of HNO_3 make the scheme of limited use for Mo and Ca recovery. A literature review shows that HNO_3 leaching might be used more effectively for molybdenite MoS_2 or metallic Mo treatment [20–24, 28]. Therefore, the Mo and Ca recovery experiment was switched to HCl leaching scheme.

## Hydrochloric acid leaching scheme

In contrast to HNO_3, HCl leaching scheme offers different initial decomposition states. In HNO_3 leaching, the CM was directly changed to solid molybdic acid, but in HCl leaching, the CM was dissolved making a very acidic yellowish solution (pH < 0) according to the following reaction.

$$CaMoO_4 + 6HCl \rightarrow H_4[MoCl_2O_4] + CaCl_2 + 2H_2O. \quad (4)$$
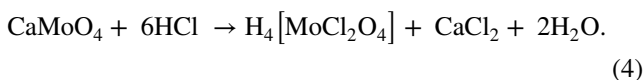
Separation of Mo and Ca can be performed by converting the yellowish solution to a solid PAM and $CaCl_2$ solution by adjusting pH. However, the concentration of Mo in the solution should precisely be considered before making PAM, because Mo has a complex chemistry due its various oxidation states. The nature of aqueous species or precipitates is predominantly determined by the concentration of Mo and pH value of the solution. In addition, as the concentration and pH change, the predominant species also change and, hence, the reaction path is also expected to change. So, it is important to know the oxidation states of Mo at specific pH values before separating Mo from the hydrochloric leached solution of CM. At pH 1.8 ± 0.2, complete acidification of MoO_4^{-2} occurs and maximum precipitation efficiency of Mo

is expected [21]. Therefore, an efficient precipitation of Mo with NH_4OH was expected at pH 1.8 ± 0.2 in the present study. The following reaction occurs for the precipitation of PAM at pH 1.8 ± 0.2.

$$H_4[MoCl_2O_4] + 10NH_4OH \rightarrow (NH_4)_2Mo_4O_{13} \downarrow \\ + 8NH_4Cl + 13H_2O. \quad (5)$$
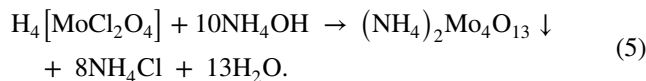
During the separation of Mo as PAM and Ca as $CaCl_2$ solutions from the leached CM, some Ca and Mo ions are present in solid PAM and $CaCl_2$ solution, respectively. Therefore, the PAM was again dissolved in the diluted NH_4OH solution and the Ca ions were separated out as the precipitates of CM at pH 8. Similarly, the Mo ions present in $CaCl_2$ were separated out as the precipitates of CM at pH 8. The intermediate CM obtained from the solutions was separately collected and not included in the final RYE calculations because of the relatively less purity.

Furthermore, this study was focused on minimizing the amount of intermediate CM to increase the RYE of final products. For this reason, CM leaching with an excessive amount of HCl than required and a range of PAM aging time in the mother solution were systematically studied. The excess amount of HCl to leach CM ranged from 15 to 55%. However, a correlation between CM leaching with excessive HCl and the amount of intermediate CM formation was not observed (Fig. 1). On the other hand, the PAM aging time substantially affected the amount of intermediate CM in AM and $CaCl_2$ solutions (Fig. 2). The amount of intermediate CM increased with the increment in PAM aging time. It was minimum (2.2%) when PAM aging time was less than 5 min and was maximum when PAM aging time was 350 min. A previous report has suggested that PAM needs to be dissolved immediately after the precipitation to get high RYE
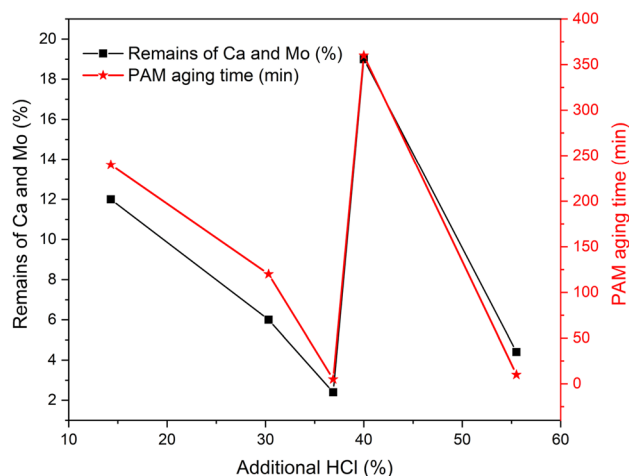

Fig. 1 Remains of molybdenum in $(NH_4)_2MoO_4$ and $CaCl_2$ solutions with excessive HCl than required theoretically and PAM aging time
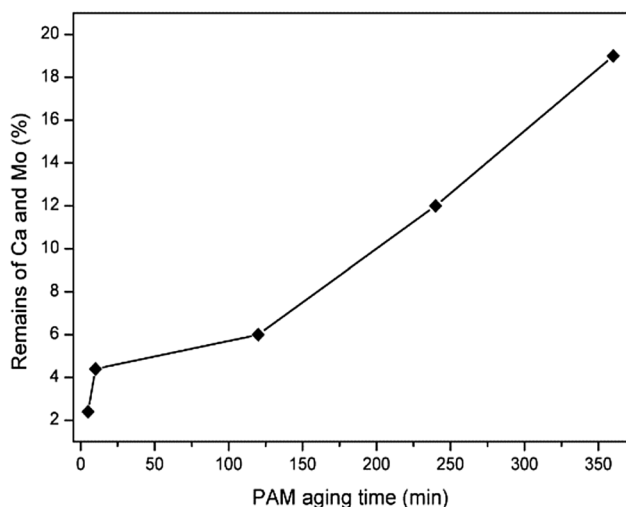
Fig. 2 Remains of molybdenum in $(NH_4)_2MoO_4$ and $CaCl_2$ solutions with different aging times of PAM in the mother solution

[26]. In addition, the concentration of Mo before PAM making should not be higher than 60 g/L, otherwise Mo may precipitate out in the form of amorphous anhydrous PAM which does not completely dissolve in acidic or basic solution [20, 24]. It might be explained by the presence of different predominant species of Mo in strong acidic solution. Lee et al. [29] have reported that at pH 0, 70% of Mo (IV) remains in the form $H_6Mo_2O_8^{2+}$ and the other remains as $H_3MO_4^+$, and at pH −1, Mo (VI) forms anionic complexes with chloride ion.

The final products were confirmed, before RYE calculation, by comparing the XRD phases with standard reference phases of $CaCO_3$ (ICSD code no. 01-085-0849) (Fig. 3) and MoO_3 (ICSD code no. 01-075-0912) (Fig. 4). The XRD phases of Mo final product showed the presence of three
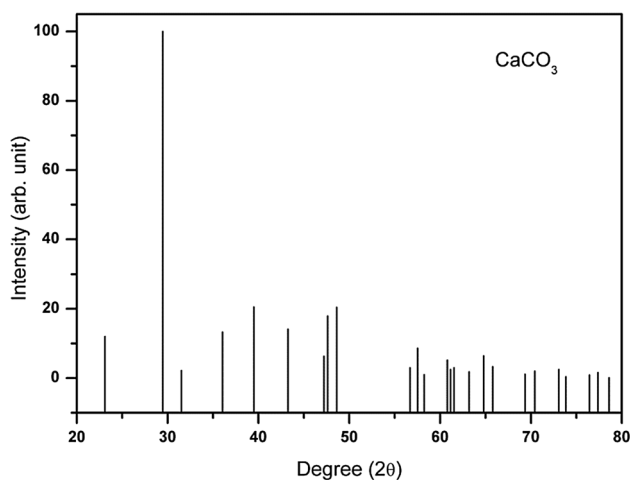
Fig. 3 XRD phase of synthesized $CaCO_3$
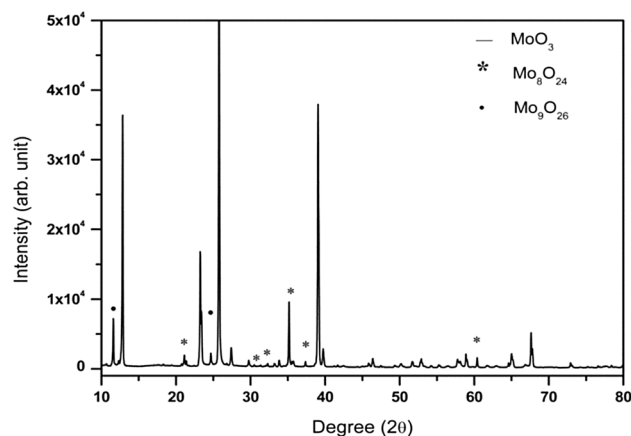
Fig. 4 XRD phase of annealed ammonium poly-molybdates at 675 °C

different compositions MoO_3, Mo_8O_{24} and Mo_9O_{26} (Fig. 4) which was possibly due to the insufficient oxygen availability during annealing [30, 31]. However, the three compositions contained approximately 66% of Mo in each. Therefore, the yield efficiency of Mo was calculated based on 66% of Mo presence in the final products. The RYE of Mo and Ca, in the present study, was increased to above 98% when aging time was less than 5 min and reduced to below 90% when aging time was 350 min. The decrement in RYE that is, increment in intermediate CM, with the increased aging time might be due to the tendency of Mo and Ca to restore their equilibrium in the solution or production of Mo and Ca ions from the decomposition of some PAM. A total of 2.2% of Ca and Mo was recovered as an intermediate CM from the calcium chloride and AM solutions, respectively, for the best RYE when PAM was aged for less than 5 min. The 2.2% intermediate CM that remained in calcium chloride and AM solutions could be of great advantage to purify the solutions, since impurities co-precipitate with it [27]. The recovered Mo and Ca could be an alternative source to grow crystals for the AMoRE project, if the products contain a low concentration of radioactive impurities. The applied recovery scheme offers a rapid and efficient method for large-scale recovery of Mo and Ca as compared to ion-exchange chromatography and solvent extraction [18].

ICP-MS analysis

Due to the limitations of HNO_3 leaching scheme described above, the reduction of radioactive impurities was measured only for HCl leaching (Table 1). The reduction in the concentrations of elements like Ra, Th and U is of great significance for decreasing the radioactivity background which can mimic the Q value of 0νββ decay of ^{100}Mo [32]. Since the concentration of Ra could not be measured efficiently using ICP-MS, and Ba, Ra and Sr belonged to the same group in

Table 1 Concentration of impurity elements and decontamination factors

	Concentration of elements (ppb)				
	Sr	Ba	Pb	Th	U
Initial CMO powder	968	329	40	0.34	2.17
Final molybdenum oxides	2567	655	9	0.012	0.212
DF of final molybdenum oxides	0.52	0.69	6	36	14
Commercial MoO_3 (99.95% purity)	24	2829	107	0.09	7
Final $CaCO_3$ powder	15	5	< 1.7	< 0.018	0.20
DF of final $CaCO_3$	129	135	> 48	> 37	22
Commercial $CaCO_3$ (99.997% purity)	5700	1400	58	< 1	1

CMO calcium molybdate, *DF* decontamination factor

periodic table, the concentration of Ba and Sr was measured to estimate the concentration of Ra. The ICP-MS analysis of Ba, Pb, Sr, Th for initial and final products is presented in Table 1. Decontamination factors were calculated using the following equation.

$$\text{Decontamination factor (DF)} = \frac{C_{\text{Mo,f}}}{C_{\text{imp,f}}} \times \frac{C_{\text{imp,i}}}{C_{\text{Mo,i}}}, \qquad (6)$$

where $C_{\text{Mo,i}}$, $C_{\text{Mo,f}}$, $C_{\text{imp,i}}$ and $C_{\text{imp,f}}$ are the concentrations of Mo in the initial and the final products, and concentrations of impurities in the initial and the final products, respectively. The standard uncertainties of ICP-MS measurement were estimated to be about 10% for Sr, Ba and Pb and about 15% for Th and U; the concentrations were calculated using calibration plotted with standards.

Decontamination factors of Pb, Th and U, after recovering Mo as molybdenum oxides, were 6, 36 and 14, respectively. It indicated that the concentrations of radioactive impurities could be reduced during the recovery process. Reduction in the concentration of such impurities in molybdenum oxides might be due to their dissolution in the acidic $CaCl_2$ solution [33] and separation during PAM filtration as well as during separation of intermediate CM. The comparative analysis of concentration of impurities in commercial MoO_3 (99.95% purity grade) and recovered molybdenum oxides suggested that the concentrations of impurities in the recovered powder were less than in the commercial one except for Sr and Pb (Table 1).

Comparative measurement of the concentration of impurities in the recovered and commercial $CaCO_3$ (99.997% purity grade) powders was done using ICP-MS. Decontamination factors for Sr, Ba, Pb, Th and U were 129, 135, > 48, > 37 and 22, respectively (Table 1). Instrumental detection limit was observed in ICP-MS for Pb and Th. Analysis of the ICP-MS data indicated that during $CaCO_3$ synthesis, most of the impurities remained in the waste solution. The analysis of impurity concentration in two powders indicated that the recovered powder was purer than the commercial one. High purity of $CaCO_3$ is of great importance for quality CM crystal growing as well as for the impurity carrier, specially, to co-precipitate Ba, Sr, Th and U [27].

Conclusions

Recovery of Mo and Ca from calcium molybdate crystal wastes was carried out by adopting HNO_3 and HCl leaching schemes in a controlled environment (Class 1000 Cleanroom) to avoid cross-contaminations and reduce the concentration of impurity elements. The HCl leaching scheme was found to be more promising to recover Mo and Ca from the crystal wastes than the HNO_3 leaching scheme. The RYE of Mo and Ca was dependent on the concentration of respective free ions present in $CaCl_2$ and $(NH_4)_2MoO_4$ solutions, respectively, after separating Mo and Ca from the leached solution of $CaMoO_4$ in HCl. The concentration of free ions was increased with the increasing aging time after complete PAM precipitation. The result suggested that an immediate dissolution of PAM is a key factor to get a high (> 98%) RYE for both elements in the final recovered products. Comparative studies of the impurities present in the molybdenum oxides powder recovered in this study and a commercially available 99.95% purity grade MoO_3 powder showed that the concentration of impurities (except Sr and Pb) could be reduced in the recovered products. Similarly, a significant reduction of the impurities like Ba, Sr, Pb, Th and U was found in the final $CaCO_3$ powder recovered as compared to the commercially available 99.997% purity grade powder. The results suggested that the method adopted in the present study could be useful to recover Mo and Ca for different uses, including the AMoRE project. On the other hand, the HCl leaching scheme is easy to run and does not require special instrument and reagents. The proposed scheme could be a more appropriate option for rapid recovery of a huge amount of Mo and Ca as compared to the other techniques like solvent extraction and ion-exchange chromatography.

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