

Mechanochemical synthesis of the copper autunites—a new route to remediation of potentially toxic elements

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Abstract

This paper focusses on the potentially toxic elements (PTE), uranium (U) and arsenic (As), which are both of concern in many developing nations that have active mining histories. U and As are toxic and carcinogenic, with U also being radioactive. In some ex-mining sites where these two contaminants co-exist (e.g., at the South Terras Mine, UK and the Zoige deposit, China) the untreated mine tailings have weathered and formed secondary mineral phases such as metatorbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and metazeunerite ($\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$). These minerals (part of the autunite group) are highly stable phases, and their formation has thus acted as a natural remediation solution and prevented U and As contamination from migrating through the surrounding environment.

In this research, we describe a novel method for the synthesis of metatorbernite and metazeunerite from laboratory reagents, which we suggest could be a promising treatment method for U- and As-containing mining wastes. The method we describe uses mechanochemical techniques, which eliminate the need for a solvent and is compatible with existing infrastructure in the mining industry (e.g. grinding and milling facilities). We discuss the method development and directions for future work, highlighting that the successful development of this technique could have significant societal impacts, particularly in developing regions with poor waste management. Our ultimate aim is to develop a sustainable remediation strategy that can be easily scaled up and applied to other hazardous solid wastes to markedly reduce latent environmental and health risks.

Keywords: remediation, mechanochemistry, uranium, arsenic

1 Introduction

1.1 Background

The issues with mine tailings and the need to develop innovative, low cost and sustainable remediation solutions for potentially toxic elements.

The potentially toxic elements (PTE) uranium (U) and arsenic (As) are of concern in many developing nations that have active mining histories, such as Namibia. U and As waste streams have caused considerable concern in Namibia for both human health and the surrounding environments (Chareyron, 2014; Abrahams et al., 2013). For instance, a U-containing waste stream, produced by a (now closed) uranium mine, is comprised of mine tailings and waste rocks. The tailings have been left exposed and uncovered, and there are growing concerns that natural weathering could cause U leaching into the environment, as documented in the Rössing mine (Chareyron, 2014). Uranium is only weakly radioactive and its primary health concerns arise from its chemical toxicity. Renal toxicity has been described as the main symptom of U exposure (Guéguen & Frerejacques, 2022), with nephritis (inflammation of the kidneys) identified as the primary chemically induced effect, regardless of exposure route (WHO, 2012). Therefore, U contamination is a global health concern (WHO, 2017). As a result of its chemical toxicity, U is subject to safety limits in the environment, with the WHO and the US Environmental Protection Agency (EPA) setting a safe level for drinking water of 30 µg/L (US EPA, 2009; WHO, 2012).

The As-containing waste stream, used in this study, is currently being produced as a by-product from the smelting of polyvalent copper ores. Previously, the As waste was refined in Namibia and a small portion sold for use as a pesticide in East Asia, until the practise was phased out following advice from an EU based multi-lateral institution following the World Health Organisation guidance (WHO, 2019). Treatment options being assessed include vitrification and traditional disposal in lined facilities – however cost and sustainability issues associated with these are complex. As has been identified by the United Nations (UN) as one of the top 10 contaminants of urgent concern (UNEP, 2020a). As is acutely toxic to humans and long-term exposure can cause a number of cancers (skin, lungs bladder, kidney; UNEP, 2020a). In villages located close to the As waste site, elevated As in urine, from historical As contamination, have been raised as a concern (Masinja 2012).

The extremely negative impacts from waste streams that contain PTEs are already apparent. Innovative, low cost and sustainable remediation solutions are urgently needed. We suggest that the use of mechanochemical methods to remediate solid waste streams is one possible strategy to pursue.

1.2 Mechanochemistry

Mechanochemistry can be defined as a solid-state process whereby a chemical reaction is initiated by mechanical means (Boldyrev 2006), i.e. a technique that applies mechanical stress and pressure in order to facilitate a chemical reaction. Over the last 100 years it has been used in many different applications such as mechanical alloying, extractive metallurgy and heterogeneous catalysis (Balaz et al. 2013). The technique has recently gained in popularity for its potential to eliminate the need for solvent in processes and the possibilities in the formation of new materials (Ranu & Stolle 2014).

Mills (planetary and ball) are the most commonly used equipment for realising the mechanical treatment of solids. The use of mills is common in many industrial processes, such as processing of ores for extraction in mining and hydrometallurgy or processing of reagents in cement clinker manufacture. Grinding, is primarily used to reduce particle size to maximise surface area to increase reactivity. However, due to the mechanical stresses and pressures involved during grinding and milling processes, reactions can also occur.

Hydrometallurgy or extractive metallurgy make use of solid-liquid reactions or mechanical activation processes to increase selectivity and efficiency in the leaching of elements of interest from ores and minerals. (Kumar et al. 2000, Boldyrev 2006, Balaz et al. 2013). Further to hydrometallurgy, there is a wide range of industrial processes in which mechanochemistry plays an important role, this includes production of catalysts, functional ceramics, materials for H storage, medicines, pigments and catalysts. As well as the formation of new materials with important applications, investigations into mechanochemical activation for the remediation of waste are also being carried out. For instance, mechanical treatment of halogenated materials to form recyclable products (Zhang 2001), mechanical treatment of clays to extract phenol from aqueous solutions (Lapides 2000) or for water purification from radionuclides. The encapsulation of PTEs through mechanical activation to form new stable remediation materials is an area worth exploring.

1.3 The autunite family of minerals

Autunite minerals ($(M(UO_2)_2(XO_4)_2 \cdot nH_2O)$; $M^+ = H_3O^+, K^+, Na^+, NH_4^+, Ba^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}$; $X = P, As$) have been recognised as important phases for controlling U mobility in the environment due to their extremely low solubility under circum neutral pH conditions. The precipitation of autunite minerals is therefore significantly beneficial for U remediation. Autunite minerals have been shown to be stable in the environment for circa 150,000 years (Jerden and Sinha, 2003), which is especially relevant when compared to other remediation techniques, such as bioreduction, that can stop being effective as soon as addition of the required nutrient amendment has ceased (Suzuki et al., 2016).

Currently, the treatment of aqueous U contamination uses phosphate permeable reactive barriers (PRBs) which involves intersecting a U contaminated groundwater plume with an available source of phosphate (e.g apatite $Ca_{10}(PO_4)_6(OH)_2$). Calcium (meta-)autunite ($Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$) is the most common precipitate at

PRBs because Ca^{2+} is abundant in apatite minerals (Bostick et al., 2000). However, as autunite minerals can support a range of cations (e.g., H_3O^+ , K^+ , Na^+ , NH_4^+ , Ba^{2+} , Cu^{2+} , Mg^{2+} , Mn^{2+}) the precipitation of other autunite phases has also been observed, particularly chernikovite [$\text{H}_3\text{O}(\text{UO}_2)(\text{PO}_4) \cdot n\text{H}_2\text{O}$], saléeite [$\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$], and sodium autunite [$\text{Na}(\text{UO}_2)(\text{PO}_4) \cdot n\text{H}_2\text{O}$] (Bostick et al., 2003; Mehta et al., 2014).

The Cu-bearing autunite phase, metatorbernite [$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] (MT), has shown particular promise as a U remediation material due to the common co-occurrence of Cu alongside U ores (IAEA, 2018). MT is more thermodynamically favourable than the majority of the other autunite minerals (Dzik et al., 2017, 2018). MT is also known to be more stable than other uranyl phosphates (Gorman-Lewis et al., 2009; Shvareva et al., 2012), uranyl oxyhydrates, uranyl carbonates, uranyl silicates (Shvareva et al., 2012), and uranyl vanadates (Spano et al., 2017), making MT among the most stable and least mobile U phase in the environment.

For many autunite minerals, As can occur in place of P to produce an analogous phase: *i.e.*, $\text{M}^{2+}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Locock et al., 2003, 2004). In the case of MT, its arsenate analogue is metazeunerite (MZ), which has the formula $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Locock and Burns, 2003). MZ also has a high thermodynamic stability and so too represents a promising remediation material for U, as well as As (Dzik et al., 2018). U and As are frequent co-contaminants owing to the common co-occurrence of U and As-orebodies (e.g. uraninite and arsenopyrite). MZ has been found to naturally precipitate in many contaminated mine sites, such as the South Terras Mine (Cornwall, UK) and in the Zoige deposit (Ruoergai County, Sichuan, China), creating a ‘natural’ remediation solution and preventing U and As contamination from migrating through the environment. (Corkhill et al., 2017; Kulaszewska et al., 2018, 2019, Zhou et al., 2019)

1.4 This paper

The development of novel, low costs and simple remediation strategies for solid waste streams is urgently required, especially in mining jurisdictions. One area that requires further exploration is the use of mechanochemistry/mechanical activation to form remediation materials. This is attractive as it avoids use of solvents, which can create further waste storage/removal problems and, as PTEs can sometimes become more mobile in solution, obviates this risk. Further, the possibility of combining waste streams to form one product for disposal is attractive both economically and environmentally.

The proposed strategy we present here, using mechanical activation processes, could be advantageous for the mining industry, particularly for solid minetailings or stockpiles containing U or As. Using on site infrastructure, e.g. the grinding and milling facilities, to produce stable products with encapsulated PTEs, will allow the waste problem to be tackled on site. This avoids either shipping the waste to remediation plants, which is expensive and potentially hazardous, or leaving the problem at the mine site, which is environmentally damaging and hazardous to health and compounds mining closure and legacy risks.

To develop new remediation materials, careful design is required and this involves controlled laboratory experiments. Here we have opted to investigate remediation of U and As, which links with extensive previous work carried out in our group, focusing on the formation, structure and stability of mineral and synthetic analogues of the autunite phases MT and MZ. (MacIver-Jones et al. 2021, 2022, Kulaszewska et al. 2018, 2019) We have carried out proof of concept work into the formation of MT using mechanochemical activation of the same starting reagents, as was used in the solution synthesis experiment for the precipitation of MT. (MacIver-Jones 2022)

We now have broadened this study to investigate phase formation of MT and MZ using mechanochemical methods, investigating the influence different U, Cu, and As - containing reagents may have on the phases formed. In this paper, we describe a novel solid-state synthesis method for the copper-autunites, metatorbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$; MT) and metazeunerite ($\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, MZ) using mechanochemical techniques, with proven effectiveness using a real-world waste sample. We propose that

mechanochemical synthesis could facilitate the formation of MZ from the U and As solid waste streams without producing liquid waste via the use of an acid solvent, leading towards a goal of combining waste streams into one product for disposal. In this paper we discuss the method development and directions for future work.

2 Materials and methodology

2.1 Synthesis

The materials described in this paper were synthesised using mechanochemical methods, which was hand grinding in a mortar and pestle. The reagents used for the synthesis were mostly lab reagents, along with one sample of waste, details of which are shown in Table 1.

Syntheses were conducted by adding stoichiometric quantities of the reagents, as listed in Table 1, to form 0.1 g of the target phase (e.g. either MT or MZ), to an agate pestle and mortar. The reagents were ground together for approximately 10-15 minutes until the mixture became a dry powder. In all cases, a bright green homogenous product was formed.

Table 1 Reagents used for mechanochemical synthesis of autunite materials

Reagent name	Reagent formula	Reagent source
Copper nitrate trihydrate	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	Acros organic 99%
Uranyl nitrate hexahydrate	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Breckland scientific 98%
Uranyl acetate dihydrate	$(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	Hopkin & Williams 95%
Uranyl sulfate hydrate	$(\text{UO}_2)(\text{SO}_4) \cdot 2.5\text{H}_2\text{O}$	BDH Chemicals Ltd. 97%
Sodium dihydrogen phosphate	NaH_2PO_4	Sigma-Aldrich 99%
Potassium hydrogen phosphate	K_2HPO_4	Thermo scientific 99%
Ammonium hydrogen phosphate	$(\text{NH}_4)_2\text{HPO}_4$	Alfa Aesar 98%
Arsenic pentoxide	As_2O_5	Sigma-Aldrich 97%
Arsenic trioxide	As_2O_3	Waste
Calcium hypochlorite	$\text{Ca}(\text{ClO})_2$	Sigma-Aldrich 97%
Phosphorous pentoxide	P_2O_5	Sigma-Aldrich 97%

2.2 Materials characterisation

The products from the synthesis were characterised via laboratory X-ray Powder Diffraction (XRPD), Fourier Transform Infrared Spectroscopy (FTIR) to identify the crystalline phases present, and Scanning Electron Microscopy (SEM) to investigate crystallite morphology.

X-ray Powder Diffraction (XRPD) is a powerful technique used to identify the presence of crystalline phases. It is known that every crystalline material has a unique XRPD pattern. The Inorganic Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) houses ~300,000 XRPD patterns (Gates-Rector & Blanton, 2019). The observed data can be compared to known XRPD patterns which are housed in the ICDD-PDF to allow the phases present to be identified.

Laboratory XRPD data were collected using a Bruker D2 Phaser powder diffractometer (D2) in reflection geometry using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) equipped with a LynxEye detector. Powdered samples were mixed with acetone then deposited as a thin layer onto a zero-background silicon (911) substrate. The

samples were then covered with a Mylar thin film (Chemplex) to prevent spillage of radioactive material. Data were collected at room temperature over the 2θ range $5^\circ < 2\theta < 60^\circ$ with a step size of 0.03° and a total data collection time of 14 minutes. Phase identification was carried out by comparing the XRPD datasets to database entries in the ICDD-PDF database using the ICDD PDF-4+ software.

Fourier Transform Infrared (FTIR) spectroscopy can be used to confirm the presence of functional groups in a material, for instance, phosphate, arsenate, nitrate. It is a very sensitive technique and does not require a material to be well crystalline to produce a spectrum. Analysis of FTIR spectra complements the analysis of XRPD data. FTIR spectra were collected on powdered samples using a Perkin Elmer FTIR Two instrument over a wavenumber range of $4000 - 400 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1} .

Scanning Electron Microscopy (SEM) was used to acquire images of some of the synthesised phases. This was to allow information on the morphology and microstructure of the phases to be determined. SEM images were collected using a Carl Zeiss SIGMA HD VP FEG-SEM instrument with an Oxford Instruments AZtecEDS system. Data were collected using an operating voltage of 10 – 15 kV. Samples were prepared by sprinkling powders onto a carbon sticky pad which was mounted onto an aluminium sample stub. Excess powder was blown off using compressed air and the samples were coated in gold.

3 Results

Table 2 shows the phases formed from reaction of the different starting reagents as identified by XRPD. The observed data and the best fits to standard XRPD patterns, alongside the FTIR spectra collected on the different materials are presented in Figures 1 - 5.

Table 2 Phases formed from mechanochemical synthesis of autunite materials using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and other lab reagents (metatorbernite $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ (MT), metazeunerite $[\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$ (MZ))

Target phase	Uranium source	Phosphate/arsenate source	Phases identified as present by XRPD
MT	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	NaH_2PO_4	MT, NaNO_3
MT	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	K_2HPO_4	MT, KNO_3
MT	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{HPO}_4$	MT, NH_4NO_3
MT	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	P_2O_5	MT, $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
MT	$(\text{UO}_2)(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$	NaH_2PO_4	MT, $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{UO}_2)(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, NaNO_3 , $(\text{UO}_2)_3(\text{SO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$
MT	$(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	NaH_2PO_4	MT, $(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, NaNO_3
MZ	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	As_2O_5	MZ, $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
MZ	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	As_2O_3	MZ, $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
MZ	$(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{As}_2\text{O}_3 + \text{Ca}(\text{ClO})_2$	MZ, $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

3.1 Testing different phosphorous containing reagents in the formation of MT

Figure 1a shows the XRPD data collected on the formed phases through reaction of uranyl nitrate hexahydrate, copper nitrate trihydrate and different phosphate reagents (Na^+ , K^+ , NH_4^+ , hydrogen phosphates). This part of the study has been submitted to Chemical Communications as a proof-of-concept

study, to show MT can form through simple grinding of reagents. When using laboratory reagent starting materials, and in the presence of other cations that are also compatible with the autunite structure (K^+ , Na^+ , NH_4^+), the targeted Cu-autunite phase (MT) was the primary phase formed. This indicates a high reaction efficiency and suggests that MT is the most stable phase under the mechanochemical conditions described. The impurity phases identified as present were the metal nitrate salts (MNO_3 ; $M = K^+$, Na^+ , NH_4^+). These nitrate salts will have formed from reaction of the spectator ions in the reaction mixture, for example K^+ , Na^+ or NH_4^+ from the phosphate reagents and nitrate from the uranyl nitrate and copper nitrate reagents.

Continuing on from this proof-of-concept study, other variables, in terms of reagent used were investigated. Replacing the phosphate reagent with P_2O_5 was attempted and while MT was shown to be present (Figure 1a green), it was found that more of the starting reagent, uranyl nitrate hexahydrate, was present than when the phosphate reagents were used.

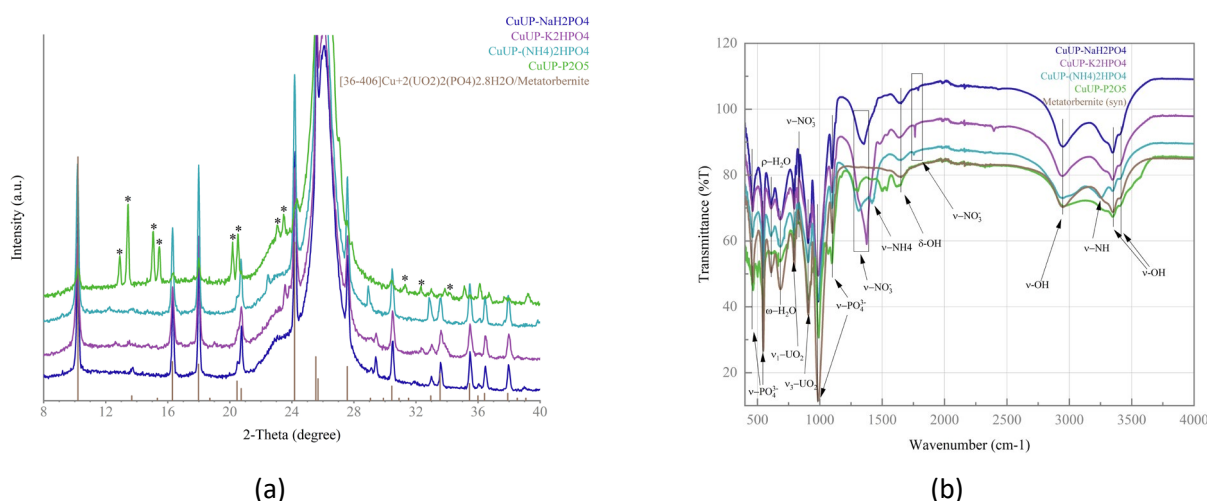


Figure 1 (a) XRPD data collected on samples prepared using different phosphate sources: NaH_2PO_4 (blue), K_2HPO_4 (purple), $(NH_4)HPO_4$ (teal), P_2O_5 (green). Brown sticks represent the standard XRPD observed reflections for MT (ICDD-PDF [36-406]), asterisks (*) represent the XRPD observed reflections for $(UO_2)(NO_3)_2 \cdot 6H_2O$ (ICDD-PDF [72-2205]) (b) FTIR spectra collected on samples prepared with different phosphate sources: NaH_2PO_4 (blue), K_2HPO_4 (purple), $(NH_4)HPO_4$ (teal), P_2O_5 (green), standard MT (brown)

3.2 Testing different uranium containing reagents in the formation of MT

The effect different sources of uranium containing salts (Table 1) had on the phase(s) formed was also investigated. For these experiments, copper nitrate trihydrate and sodium dihydrogen phosphate were mixed with either uranyl nitrate hexahydrate, uranyl sulfate hydrate or uranyl acetate dihydrate. The XRPD data and FTIR spectra collected on the phases formed from these experiments are shown in Figure 2. It was observed that the amount of MT phase formed and the crystallinity of the phase differed depending on the uranyl salt used. For the phases formed when either uranyl acetate or uranyl sulfate was used, it was found a large amount of the starting uranyl salt reagent was present, as well as several other impurity phases, that had formed during the grinding (Table 2). In comparison, the reaction using uranyl nitrate hexahydrate, identified MT as the major phase present with only a small amount of $NaNO_3$ as an impurity phase. The $NaNO_3$ will have formed from reaction of the spectator ions in the reaction mixture, e.g. Na from the sodium dihydrogen phosphate reagent and nitrate from the uranyl nitrate and copper nitrate reagents.

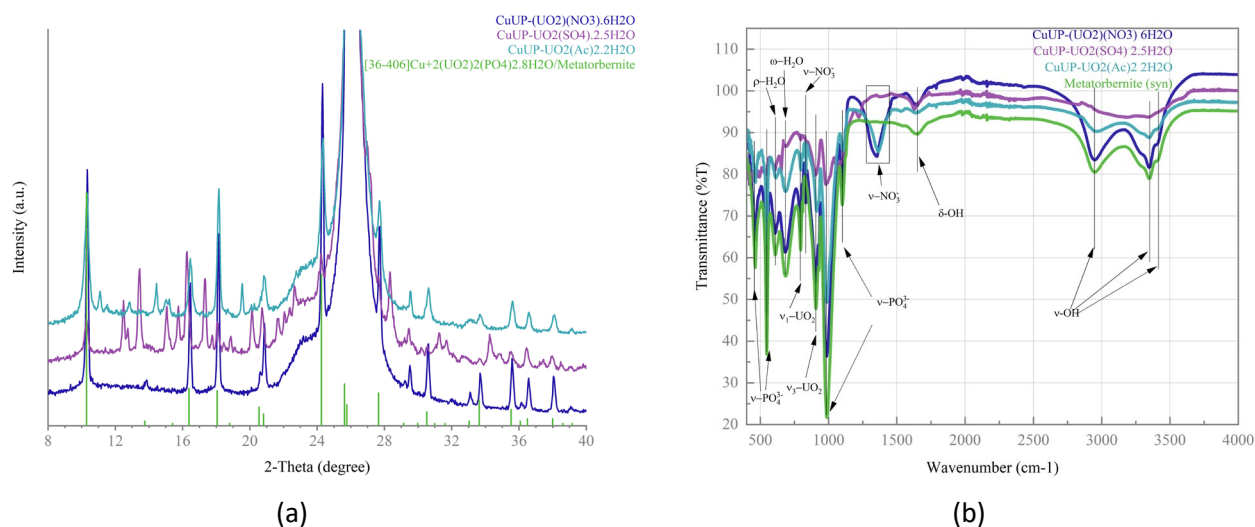


Figure 2 (a) XRPD data collected on samples prepared using different uranyl sources; $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (blue), $(\text{UO}_2)(\text{SO}_4) \cdot 2.5\text{H}_2\text{O}$ (purple), $(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (teal). Green sticks represent the standard XRPD observed reflections for MT (ICDD-PDF [36-406]). (b) FTIR spectra collected on samples prepared with different phosphate sources: $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (blue), $(\text{UO}_2)(\text{SO}_4) \cdot 2.5\text{H}_2\text{O}$ (purple), $(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (teal), standard MT (green)

3.3 Stability of phases

For remediation purposes, washing of samples is not advisable, as this will generate volumes of liquid waste that will require storage or disposal. However, for this laboratory-based study, all samples were washed with deionised water and dried. This was to test the stability of the targeted MT phases in aqueous, neutral pH conditions. The resulting samples were analysed by XRPD and FTIR spectroscopy. Figure 3 presents the XRPD and FTIR data on the samples that were prepared using different sources of phosphorous, which have been washed. Those samples prepared using NaH_2PO_4 and K_2HPO_4 are now phase pure MT. The FTIR spectra show that the nitrate bands ($\sim 1300 - 1500 \text{ cm}^{-1}$) are no longer observed, confirming the NaNO_3 and KNO_3 impurity phases have been removed during washing. The crystallinity of the resultant MT phases is still high, confirming its stability under these pH conditions.

The sample prepared using NH_4HPO_4 , no longer shows the presence of the NH_4NO_3 impurity, again, this phase has been removed during washing, which is also confirmed by the FTIR spectra, with no nitrate band observed ($\sim 1300 - 1500 \text{ cm}^{-1}$). However, there are now two autunite-type phases that can be identified, MT (Brown sticks, Figure 3a) and uramphite ($(\text{NH}_4)(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$) (Red sticks, Figure 3a). In our previous work on the stability of MT under different conditions of pH, we have shown that when MT is in solution and in the presence of NH_4^+ , then cation exchange processes occur. (MacIver-Jones 2022) We propose, this has occurred during the washing of the MT phase, whereby the NH_4NO_3 dissolves, releasing NH_4^+ cations into the solution which then undergo exchange with the Cu^{2+} cations. This ion exchange process occurs as the autunite phases are layered structures, with the Cu^{2+} and NH_4^+ cations located between the layers (Figure 4). There was no evidence for exchange of Na and K with Cu in the other samples; this was also shown in our stability studies. (MacIver-Jones 2022) There is something unique about the stability of the uramphite phase, which requires further investigation.

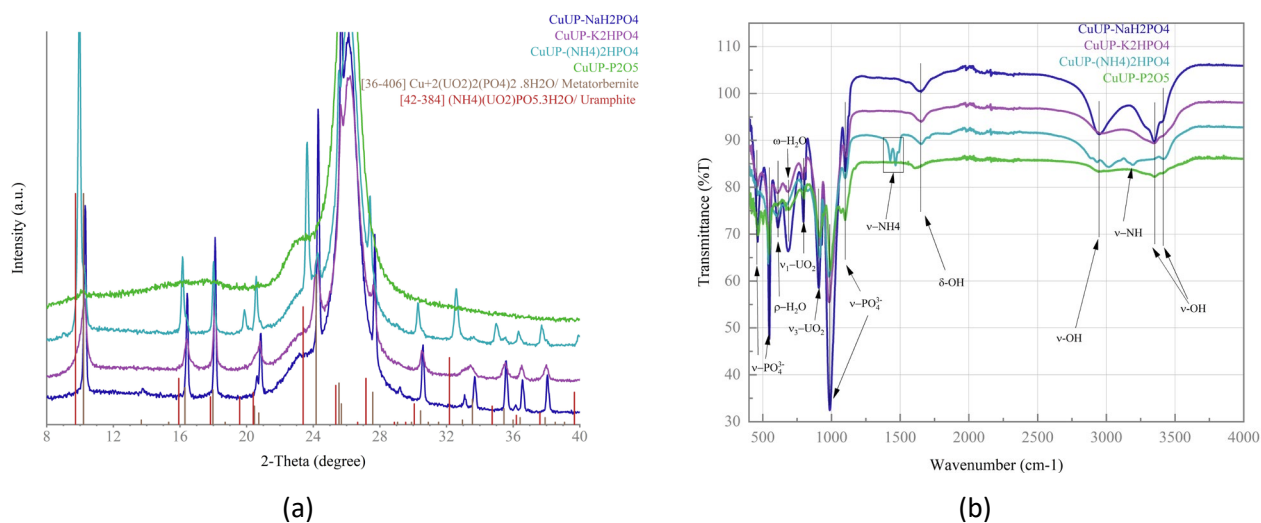


Figure 3 (a) XRPD data collected on samples prepared using different phosphorous sources after washing with deionised water; NaH_2PO_4 (blue), K_2HPO_4 (purple), $(\text{NH}_4)\text{HPO}_4$ (teal), P_2O_5 (green). Brown sticks represent the standard XRPD observed reflections for metatorbernite (ICDD-PDF [36-406]), brown sticks represent uramphite (ICDD-PDF [42-384]) (b) FTIR spectra collected on samples prepared with different phosphate sources after washing with deionised water: NaH_2PO_4 (blue), K_2HPO_4 (purple), $(\text{NH}_4)\text{HPO}_4$ (teal), P_2O_5 (green)

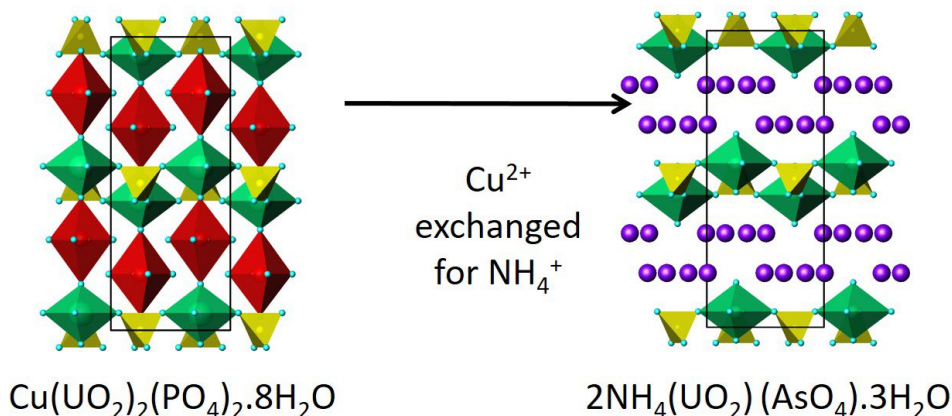


Figure 4 Possible ion exchange process occurring when MT is in the presence of NH_4^+ cations, forming uramphite $((\text{NH}_4)(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O})$

Washing of the samples prepared using different U containing salts was also carried out. The XRPD data and FTIR spectra collected on these samples are shown in Figure 5. In all cases, the impurity phases, identified as present in the original, unwashed samples, have been removed during the washing and the observed XRPD patterns show the presence of only MT. However, the observed diffraction peaks for the washed sample prepared using the uranyl acetate dihydrate, are broad, suggesting the crystallinity of the resultant phase is poor.

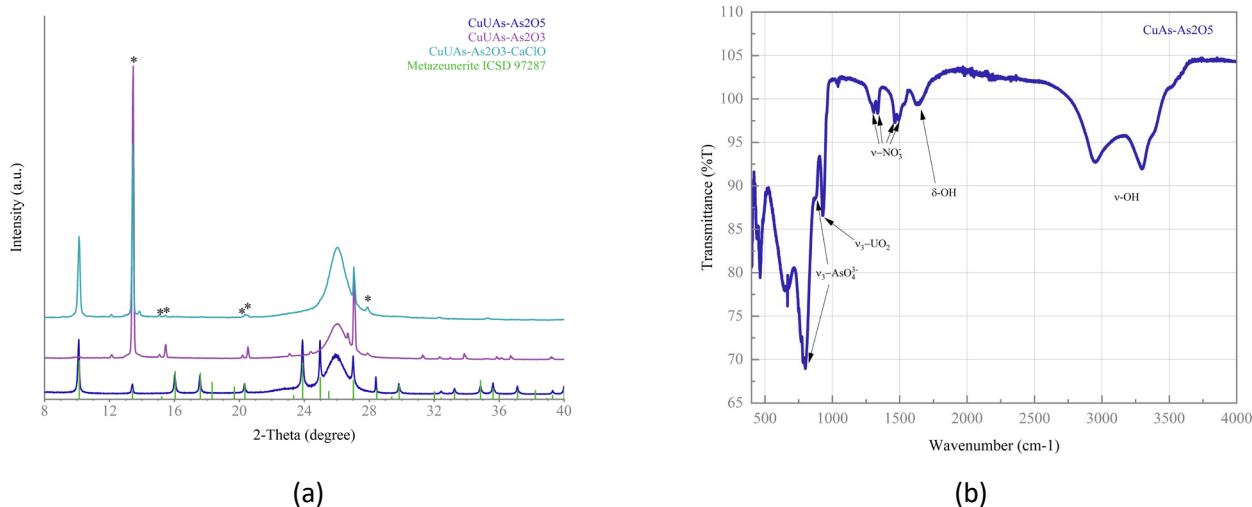


Figure 6 (a) XRPD data collected on samples prepared using different arsenic sources; As_2O_5 (blue), As_2O_3 (purple), As_2O_3 and $\text{Ca}(\text{ClO})_2$ (teal). Green sticks: standard XRPD observed reflections for synthetic metazeunerite (ICSD [97287]/ICDD-PDF 04-012-9855), asterisks (*): XRPD observed reflections for $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ICDD-PDF [72-2205]). (b) FTIR spectra collected on sample prepared with As_2O_5 (blue)

3.5 Morphology of the MT and MZ phases

SEM analysis was carried out on the samples after they had been washed to investigate crystallite size and morphology. Figure 7a shows an SEM image collected on a sample of MT, formed through grinding of uranyl nitrate hexahydrate, copper nitrate trihydrate and sodium hydrogen phosphate. The tetragonal crystallites are well formed and the morphology is typical for MT-type phases. (Vochten 1990) Figure 7b shows an SEM image of a MZ sample formed following the mechanochemical mixing of uranyl nitrate hexahydrate, arsenic pentoxide, and copper nitrate trihydrate. Similar to MT (Figure 7a), the crystallites exhibited a well-formed tetragonal shape. The MZ crystallites were larger than the MT crystallites, which may have been due to the period of maturation. The SEM study shows the samples formed through this process have good crystallinity and morphologies similar to that expected of autunite type phases. (Vochten 1990)

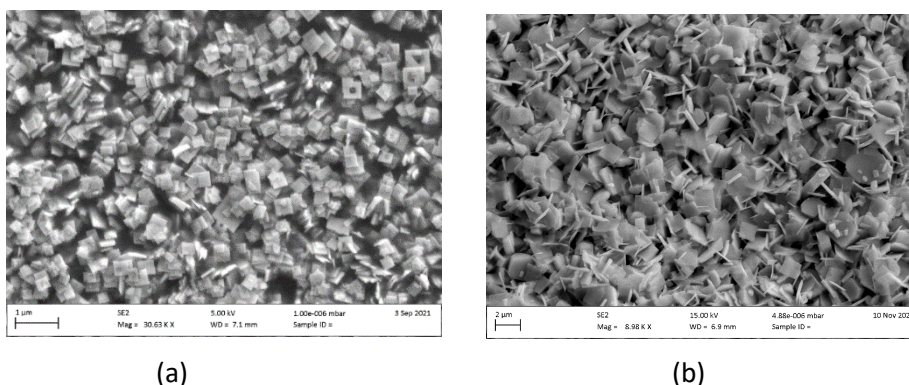


Figure 7 (a) SEM image of the well-formed tetragonal MT crystallites obtained via mechanochemical synthesis (b) SEM image of the ideal well-formed, platy tetragonal MZ crystallites formed via mechanochemical synthesis

4 Conclusion, further work and outlook

4.1 Conclusion

We have successfully shown that both MT and MZ phases can be formed using mechanochemical activation of lab reagents. The products of the reaction are often multi-phase, with either by-products of the reaction or starting reagents present alongside the autunite phases. The products were washed in deionised water, which is not a desirable step for real work applications, but it allows us to investigate their stabilities under circum neutral pH conditions. In all cases, the phases that were not MT or MZ were removed in this step.

Our studies have shown that the starting reagents do influence both the phase formation, in terms of how complete the reaction is, as well as the crystallinity of the final product. The use of uranyl nitrate hexahydrate, copper nitrate trihydrate and metal hydrogen phosphate (either NaH_2PO_4 , K_2HPO_4 or NH_4HPO_4), formed a well crystalline product with a metal nitrate impurity, which was easily removed through washing. This suggests the reaction has gone to completion. When carrying out the reaction with a different uranyl salt, $(\text{UO}_2)(\text{SO}_4) \cdot 2.5\text{H}_2\text{O}$, $(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ MT was formed, but was not the major phase present, with starting reagents remaining and other reaction products formed (e.g. uranyl nitrates, copper hydroxyl nitrates). This could either be due to these uranyl salts being less hydrated than uranyl nitrate hexahydrate or that the sulfate and acetate ions are influencing the reaction process, with other phases forming, which may be more thermodynamically stable than MT.

Formation of MZ was carried out using arsenic oxides reacting with uranyl nitrate hexahydrate and copper nitrate trihydrate. When As was in the pentavalent oxidation state, (As_2O_5), the product formed was mostly MZ, with some uranyl nitrate hexahydrate observed as present, suggesting the reaction had not gone to completion. When As_2O_3 was used as the reagent, with As in the trivalent oxidation state, only a small amount of MZ was found to form after the mechanochemistry experiment. In MZ, As is in the pentavalent state, therefore the reaction was repeated adding an oxidising agent, in this case calcium hypochlorite. On addition of the oxidising agent, more MZ was shown to form, however, the reaction had still not gone to completion, as a significant amount of uranyl nitrate hexahydrate was also observed as present in the reaction product.

4.2 Further work

In order to ensure that the mechanochemical synthesis of MT and MZ produces a stable product for safe disposal, stability tests would be required. We have a programme of work underway to study the stability of the phases under different conditions of pH and temperature. This is required to ensure the MT and MZ phases will not break down, either when in solution or at non-ambient temperatures and potentially leach out the U/As metals. We have carried out stability studies of MT and MZ phases formed using solution synthesis methods, which has shown that phosphate phases are more stable than the arsenate phases in the presence of aqueous carbonate. (Maclver-Jones, 2022) Therefore, the partial incorporation of a phosphate material into the mechanochemical mixture may help to aid overall stability of the end product. However, this needs to be explored as it is not yet clear if members of the MT-MZ solid solution, reported to exist through synthesis and in nature, e.g. at the South Terras mine, Cornwall, UK, can form via mechanochemical synthesis. (Corkhill et al., 2017; Kulaszwewska et al., 2019) As well as determining general stability fields, it would be important to establish whether the Cu-autunite product obtained via mechanochemical synthesis is more, less, or of equal stability compared to the products obtained via aqueous precipitation. (Cretaz et al., 2013)

Investigations into whether these MT and MZ phases can be formed using real waste streams is vital further work. We predict that obtaining the required U:As stoichiometry from two waste streams will be the main obstacle when using real waste samples to synthesise MZ. While one of our sources of As waste can be extremely As-rich (e.g. ~20 wt%), the concentration of U in the U-containing mining waste (carnotite) will likely be much lower as most of the ore grade material ($\geq 0.01\% \text{U}_3\text{O}_8$) will have been extracted for processing.

Future work will need to establish whether the mechanochemical synthesis of MZ can be achieved using both waste streams, and what the ideal mass ratio of each waste stream is. Other regional analogous samples of U waste (containing higher wt% U) could be sourced to provide required stoichiometric variation.

Studies into competing reactions with other ions/elements, that may be present in real waste streams, is also vital. This will allow us to explore whether a waste stream will form a cocktail of phases and inhibit the formation of the targeted MT/MZ phase. We will also investigate whether addition of a simple and cheap reagent could progress the reaction and form the targeted phase(s). Addition of a copper reagent on an industrial scale could make the method prohibitively expensive. However, it is likely that the U-containing waste stream will also contain copper as a co-contaminant, as uranium and copper ores often coexist at the same sites. If this is not the case, future work should explore whether the synthesis is successful for other phases such as Na, K, Ca-autunites, which would require much cheaper cation-containing reagents.

We need to explore whether scaling- up of this method is possible. Scaling-up would most likely require industrial ball milling in order to break up the rock in the U-waste and facilitate mechanochemical mixing on an industrial scale. This may also serve to increase the reaction efficiency, as our proof-of-concept studies suggest that a major limiting factor for reaction efficiency was the breakdown of the starting materials. We are also studying the use of other grinding methods, such as ball/planetary milling and resonant acoustic mixing (RAM) in our lab experiments.

4.3 Application to other remediation materials

If the stoichiometry of the two waste streams is too disparate (i.e., the U in the U waste stream is too dilute) to allow the mechanochemical formation of MZ, then we suggest applying the mechanochemical principle described here to target different remediation phases. For example, a promising target phase for the As waste stream could be scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Scorodite is already used as a remediation material for As waste produced during copper mining in Chile via treatment of leach solutions. (Perez et al., 2021; Valenzuela, 2018) The development of a mechanochemical synthesis route for scorodite would have significant benefits for the treatment of the As wastes in the solid state.

4.4 Outlook

Globally, the threats posed by hazardous mining wastes disproportionately impact indigenous and poor communities in developing nations, with richer countries often leaving behind toxic tailings where there are little to no environmental regulations, or even shipping wastes in to avoid costly and/or unpermitted disposal at home. (UNEP, 2017, Clapp, 2001) The UN has therefore set new goals to improve the safety of mine wastes and tailings, with an ambition of 'zero harm to people and the environment'. (UNEP, 2020b) **Innovative, low cost and sustainable remediation solutions are urgently needed to achieve this goal.** The development of mechanochemical waste remediation treatments could provide an efficient, low cost, and solvent free strategy with global application. As the sound management of chemical waste is integral to all 17 of the UN's sustainable development goals (SDGs), the successful development of this technique could have highly significant societal impacts, particularly in developing regions with poor waste management and vulnerable, exposed communities.

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