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Zirconium Molybdate Crystal Growth
and Morphological Control

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ABSTRACT

This thesis investigated the formation of zirconium molybdate (ZM) \((\text{ZrMo}_2\text{O}_7(\text{OH})_2.2\text{H}_2\text{O})\) crystals in conditions designed to reflect those found during the processing of spent nuclear fuel, in which these crystals are seen to form. Greater understanding of the formation of ZM was sought by studying the effect of many chemical species, including many known to be present in the mixture and a number of others specifically selected. The final goal was to provide means to control the creation of ZM crystals which exhibited advantageous physical characteristics. The ZM crystal morphology was found to be highly influenced by a few species which gave rise to several newly characterized novel crystal forms of ZM that exhibited interesting rheological and packing properties.
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Thank you!
from magic"

"Any sufficiently advanced technology is indistinguishable
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1 INTRODUCTION TO THESIS

OVERVIEW

This thesis contains detailed investigations of zirconium molybdate crystallization in conditions representative of irradiated nuclear fuel reprocessing systems. The work was intended to generate greater understanding of current processes, examine potential methods of resolving some of the challenges created by zirconium molybdate formation, and provide guidance for future process design. In the first instance the nuclear industry in the UK is introduced and the nuclear cycle described with focus placed on irradiated fuel reprocessing and waste treatment. The importance of zirconium molybdate is highlighted and the stimulus for the work contained within this thesis explained, before finally methods of accomplishing the undertakings are introduced and defined.
1.1 **NUCLEAR INDUSTRY IN THE UK**

Since the 1950's the main nuclear industries in the UK have been the generation of electricity and the weapons industry.\(^1\) However, many more industries use radioactive materials, including hospitals, research institutions, petrochemical, and pharmaceutical establishments. Irradiated material produced by these industries cannot be dealt with in the same manner as most toxic material because it requires special treatment to protect the public and the environment, and to prevent proliferation of nuclear technology.\(^2\)

1.1.1 **IRRADIATED MATERIAL REPROCESSING IN THE UK**

The research undertaken in this thesis was supported by the National Nuclear Laboratory (NNL) under contract from Sellafield Ltd, based at the Sellafield nuclear licensed site in north-western England. The site is home to the UK's main irradiated material reprocessing and fuel production facilities as well as various experimental and research installations. The reprocessing side deals with all levels of irradiated material, from low level disposable products which may have come into contact with radioactive material to highly radioactive irradiated nuclear fuel a product of nuclear powered electricity generation.\(^2\) The majority of the low risk irradiated material undergoes simple processing, but highly radioactive waste requires greater treatment.

The Sellafield site is owned by the National Decommissioning Authority (NDA) and is operated by Sellafield Ltd. It is one of the largest nuclear licensed facilities in the world, employing over 10,000 people and has the highest combined reprocessing-capability of any site worldwide. Sellafield was originally a Second World War munitions factory, chosen after the war as the location for \(^{239}\text{Pu}\) production for use in the British nuclear weapons program.\(^3\), \(^4\) The development of the site began with construction of the Windscale Piles, which were research only reactors used to produce
the plutonium, a product of the irradiation of $^{238}$U. Sellafield was later host to the world’s first commercial electricity generating nuclear reactor, Calder Hall, which opened in 1956.

During the construction of the first generation of nuclear installations in the UK there was little or no forethought regarding the post-operational future of the sites or how to handle any irradiated products. For this reason the nuclear industry in the UK had a legacy of historic buildings, irradiated fuel and infrastructure remaining which require safe shut-down and disposal. Future plans include the POCO of current and any future nuclear facilities and solving a number of challenges relating to reprocessing irradiated materials, which is where zirconium molybdate (ZM) is produced.
1.2 The Nuclear Fuel Cycle

The fuel currently used for nuclear powered electricity generation in the UK contains almost entirely uranium before it is irradiated. In general, UK nuclear power stations are operated by exploiting the kinetic and electromagnetic energy produced by the exothermic nuclear fission reactions of $^{235}$U, although another fissile material $^{239}$Pu is produced by neutron capture and subsequent beta emission of the relatively abundant $^{238}$U. The energy release associated with nuclear fission reactions provides heat which is used to produce the steam which drives electricity generating turbines. A nuclear fission reaction takes place when a fissile nucleus captures a neutron causing it to become unstable and split into smaller nuclei, releasing energy and often energetic thermal neutrons (Figure 1.1). Only nuclei of certain isotopes of particular elements are capable of spontaneous fission reactions and the natural abundance of $^{235}$U has made it appealing for use in nuclear power generation. Most fission reactions which occur in electricity generating nuclear fuel are triggered by impact with a thermal neutron produced during a previous fission event. Once fission has begun the number of free thermal neutrons capable of initiating further nuclear fission reactions is greater than that which would be needed to maintain the reaction. Therefore, the free neutrons flux will exponentially increase as long as there is a high enough density of fissile elements in the bulk of the fuel allowing a chain reaction to be set up wherein nuclear fission reactions become self-sustaining and producing increasing amounts of energy. In electricity generating reactions control rods are used to absorb or slow thermal neutrons allowing control of the reaction rate by moderation of the neutron flux therefore, controlling the energy produced and preventing “run-away”.

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Figure 1.1 Diagram of nuclear fission taking place by collision of a thermal neutron with a fissile nucleus (1st Generation). Fission products and 2 or 3 thermal neutrons are produced which can then go on to cause further fission reactions (ad finitum).

Magnox and oxide fuels are two types of fuel currently used in British nuclear fission reactors. The name Magnox was derived from “magnesium non-oxidizing” and refers to the alloy cladding which surrounds the natural / non-enriched uranium metal fuel rods. Although the Magnox reactor design is redundant a number of Magnox reactors still operate in the UK and there is a legacy of irradiated Magnox fuel which requires reprocessing. Low-enriched uranium (LEU) fuel composed of 3 – 5 % enriched uranium ($^{235}$U) dioxide in a ceramic matrix and is the fuel on which most commercial nuclear reactors in the UK were designed to run. Mixed oxide (MOX) fuel is similar to LEU fuel but it contains a mixture of both uranium and $^{239}$Pu obtained from either reprocessed fuel or surplus weapons grade plutonium. MOX fuel can be used as an alternative to LEU in some modern reactors.
The current approach in the UK is to replace the fuel rods in nuclear power station reactors every 3 - 5 years. After this time the fissile material in the power output of the fuel has been decreased due to significant burn-up of the fissile material and the formation of impurities which are mainly fission products and minor actinides. Once removed from reactors the irradiated fuel rods are left to cool in temporary storage ponds on the site of the reactors in which they were used, allowing the majority of the short-lived isotopes to decay. The irradiated fuel rods are then sent to Sellafield and stored in large cooling ponds to allow a further period of cooling before the fuel is reprocessed. Irradiated nuclear fuel reprocessing involves the recycling of the uranium and plutonium contents and the long-term immobilization of remaining material.

Figure 1.2 Schematic of the nuclear fuel cycle

1.2.1 Reprocessing at Sellafield

The first task of irradiated fuel reprocessing is the dissolution of the contents of the irradiated rods in hot concentrated nitric acid. Irradiated fuel rods contain around 95% useful uranium and plutonium material with fission products and minor actinides making up the remaining 5%. The next step of reprocessing is a solvent extraction process called plutonium uranium extraction (PUREX), a process which separates useful uranium and plutonium from the waste fission products and minor actinides.
The PUREX process uses odourless kerosene mixed 80 : 20 with tri-n-butyl phosphate (TBP), a complexing agent specific to uranium and plutonium. The TBP then transports the uranium and plutonium into the more dense organic phase, separating them from the remaining fission products and minor actinides in the aqueous phase.\(^9\) Ferrous sulphamate is then used to separate the plutonium from the uranium by reducing the plutonium so that it returns to an aqueous phase.\(^10\) The uranium and plutonium streams are then able to be further processed with oxide fuel generated in most cases. After the removal of uranium and plutonium the remaining material is treated as a waste stream called highly active (HA) raffinate however, the separation process is not perfect and there does remain a small amount of uranium, plutonium, and TBP in the waste stream.\(^8\)

### 1.2.2 Nuclear Industry Waste Products

Sellafield is tasked with handling the three different classes of nuclear industry waste material, categorised as either Low-Level Waste, Intermediate-Level Waste or High-Level Waste.\(^11\) Low-Level Waste (LLW) comprises items which may only be slightly contaminated with irradiated material but which therefore, cannot be treated as normal waste, and require a certain amount of processing. LLW includes objects such as protective clothing, filters, and damaged equipment which generally come from hospitals, nuclear power generation, research, and defence establishments. Processing of LLW can involve simple containment in a sealed metal drum or dispersal of dilute gaseous and aqueous wastes into the air and surface water. The majority of LLW is compacted and packaged into half-height ISO-freight containers before grouting and storage at the low level waste repository (LLWR), located a few miles south of Sellafield.
Intermediate-Level Waste (ILW) includes materials such as fuel cladding, components, resins, and sludge all of which come from sources such as nuclear power stations, processing centres, and the radioisotope industry. ILW is generally dealt with by encapsulation in a cement matrix and long term storage. The ILW containers are currently stored on the Sellafield site in purpose built over-ground stores.

High-Level Waste (HLW) exclusively comprises the parts of irradiated nuclear fuel which are not recovered for further use. After removal of U and Pu by the PUREX process the HLW stream is concentrated and immobilized by combination with glass in a process called vitrification. The product is a solid glass block containing the fission products and minor actinides which were produced during irradiation of the fuel in a nuclear reactor. The vitrified products are then sent for long term storage to allow for the decay of the waste material radioactivity.

It is seen as good practice to reduce the volume of HA raffinate prior to vitrification so that the mass of material sent for long term storage is minimized. To accomplish volume reduction the waste stream (HA raffinate) is sent for solvent evaporation. After volume reduction the acidity of the waste stream, now called highly-active liquor (HAL), is very high. A process called water-acid reduction (WAR) is then used to decrease the acidity of HAL before it is vitrified. By combination with glass in stainless steel drums the fission products and minor actinides are immobilized before they are sent to highly engineered stores pending a final repository. It is during the processing of HA raffinate and HAL where zirconium molybdate crystal growth takes place and therefore, the area which is of interest to this thesis.
1.2.3 HALES

At Sellafield volume reduction and temporary storage of the HA waste stream takes place at the highly active liquor evaporation and storage (HALES) building. HALES has three HA evaporators used to reduce the volume of HA raffinate, with the possibility of more planned. Two of the evaporators are designed to deal with Magnox waste streams and the third can deal with both Magnox and oxide waste streams. Typically the evaporators operate at reduced pressure (50mm Hg) and a bulk temperature of 50-60°C. They have a capacity of 13.7 m³ and can attain a reduction of the waste volume by a factor of 50-100.\(^8\)

Distillate from the evaporators is condensed and the acid partially recycled before the remnants are sent to the ILW line. The temperature of the evaporators is controlled by an external water jacket and internal water filled coils which can heat up and cool down the evaporators as required. The concentrations of a number of chemicals are also monitored, for example the amount of hydrazine is controlled because the thermal breakdown of ammonium nitrate releases gases which could lead to vessel pressurization and misdirection of radioactive material into uncontrolled areas.\(^13\)

![Figure 1.3 Schematic diagram of HALES showing the input of highly active raffinate going to the evaporator before it emerges as highly active liquor (HAL) which is sent to highly active storage tanks (HASTs) before being sent for vitrification.](image-url)
During volume reduction the acidity of the raffinate increases to a maximum nitric acid concentration of 12 molar. This makes the waste stream highly corrosive and WAR is used to reduce the liquid acidity in order to moderate evaporator corrosion and make the waste stream compatible with downstream processing requirement. Post-evaporator the HAL is pumped into highly active storage tanks (HASTs) were it is stored until it can be sent for vitrification.

The first generation of HASTs were relatively simple storage tanks with inbuilt cooling mechanisms. In contrast, newer models are highly engineered tanks incorporating many safety features, including mixing and the ability for in-tank evaporation to occur allowing volume reduction to continue. In-tank evaporation occurs without the need for an external heat source because the radioactivity of the HAL is such that the liquor is self-heating.

1.2.4 Waste Vitrification Plant

The final stage of HLW processing is the vitrification of the waste stream at the waste vitrification plant (WVP), Sellafield. Once the concentration criteria for a number of chemical species have been met, the HAL is transferred from HALES to the WVP where glass crizzle is added to the liquor and the mixture heated above the glass transition temperature. The molten glass and HAL mixture is then poured into stainless steel drums and allowed to cool, forming a solid block. A lid is then welded onto the canister before it is decontaminated and taken away for storage. Presently, overground stores are used for these glass blocks because a decision is yet to be made about the nature and location of long term repositories. The expectation is that they will ultimately be deep geological repositories.14
1.3 CHALLENGES FOR HALES

The concentrated nitric acid used to dissolve irradiated fuel makes HAL highly corrosive; this creates problems regarding the management of the reprocessing infrastructure including process-side thinning of the stainless steel evaporators and vessels. Temperature has a strong influence on the corrosion rate of evaporators and HASTs. Thermal models and coil inspection data have indicated that the surface temperature of the in-tank heating components increases with submerged depth. This temperature inhomogeneity has led to higher than expected corrosion rates toward the base of the evaporators and was thought to be the cause of the failure of a number of thermal coils in the bottom arrays of the evaporators. A finding which has resulted in a reduction of the expected operational lifetimes of the evaporators.

Another significant problem is the formation of solids during volume reduction and storage of HAL in part due to the fast settling nature of some of these solids and ineffectual re-suspension methods. The resulting sedimentation often causes the formation of long-lived settled-beds of solids in evaporators, HASTs, and other HALES infrastructure. The temperature of HAL is closely controlled but both the presence of settled solids and the higher temperatures present at the bottom of the vessels add to the inhomogeneity in temperature distribution. Sedimentation causes the formation of insulating blankets of solids on the base of the vessels, decreasing the heat exchange efficiency of the external water jacket. However, the heat-producing radioisotopes in the settled solid beds are often the cause of greater operational complications specifically $^{137}$Cs. Concentration of heat-producing radioisotopes in the solid phase and the subsequent sedimentation of the solids to the base of the vessels results in the formation of settled-beds which cause prolonged localized heating. Where this occurs over an
extended period of time in evaporators or HASTs it is referred to as “hot-spot” formation.

A number of strategies have been developed to combat the corrosion caused by hot-spots and settled solids. One of which was to promote the conversion of all caesium phosphomolybdate (CPM) to zirconium molybdate (ZM) for the reason that CPM is one of the principal heat producing solids in HAL a consequence of the three caesium ions in CPM, and because half of the caesium atoms present in HAL are the highly radioactive isotope $^{137}\text{Cs}$.\textsuperscript{15} Therefore, when the heat-generating $^{137}\text{Cs}$ is bound in the solid phase as CPM, there is less control of its distribution in the vessels and the $^{137}\text{Cs}$ is more likely to be present and cause increased local temperatures at the base of the vessels. However, when HAL acidity is reduced to 2 – 4 molar nitric acid prior storage the CPM begins to breakdown releasing molybdenum, phosphorous and caesium into the solution phase. This release of $^{137}\text{Cs}$ dramatically reduces the power-output of the solids in HAL, such that the energy produced by all of the solids falls from 27.62 W/Litre to 2.95 W/Litre on 100% breakdown of CPM.\textsuperscript{15} The molybdenum released during CPM breakdown almost exclusively goes on to form ZM, preventing reformation of CPM. Therefore, promotion of the conversion of CPM to ZM could be used as a chemical method of reducing the corrosion caused by settled solids.

Decreasing the likelihood of solid sedimentation or improving the re-suspension properties of HAL solids is another method which is thought would reduce the corrosion rate by decreasing the probability of long-term settled beds of solids forming. Making the settling of solids slower would improve the affectivity of the in-situ mixing methods allowing settled beds less chance to form. One method for changing the settling rate of HAL solids is to alter the morphology of the particles causing them to flow differently in suspension. Altering the morphology of the particles will also affect
the structure of any settled bed and could change the force required to re-suspend them. If the structure of the settled solids was less dense with a more open structure it would make the solids easier to break-up and re-suspend, improving HAL solids management.

In a recent study of aged simulant HAL, characterization of the solids in the product discovered ZM crystals with an unusual morphology. Typically, ZM crystals possess a cuboidal habit with straight edges and flat faces but the report observed the presence of ZM crystals with elongated wheat-sheaf morphology. The crystals were found in a batch of HAL simulant which had undergone a number of procedures intended to mimic actual HAL processing. This finding revealed that the morphology of ZM crystals could be affected and possibly tailored. The cause of the morphological change was not identified in the report but it was thought to be caused by the presence of one or more of the chemical species present in HAL. The wheat-sheaf morphology is very different from the typical cuboidal shape expected for ZM. When considered against the cuboidal crystal the elongated nature of the wheat-sheaves were thought likely to alter and possibly improve the sedimentation rate and re-suspension properties of ZM solids. Therefore, if the reason for the observed change in morphology could be identified and the effect controlled or exaggerated a possible route for improved corrosion management could be available.

1.3.1 Scope of this Thesis

In 2001, the nuclear installations inspectorate produced a report on the storage of liquid high level waste at Sellafield containing 22 recommendations. Number 20 recommended developing a permanent solution to the problem of pipework blockages and expressed concerns over the lower than expected perceived lifetime of the
evaporators. Both of which were largely, or in part, caused by solids formed during reprocessing.

The work contained within this thesis was focussed on investigating the crystallization of ZM, a micro-crystalline material which forms during the reprocessing of nuclear waste. The task set out by Sellafield, was to understand the general mechanism of ZM crystallization and to work within the constraints of HALES procedures to improve the manageability of ZM solids in HAL, and as a consequence improve the settling properties of all the solids in HALES. The tendency for fast settling was seen as the main problem caused by ZM and other HAL solids, improvement of this aspect of ZM is seen as the major industrial aim for this work. The morphology of ZM crystals in simulant HAL has been seen to be changeable and if this modification could be understood and controlled it could possibly be used to change the settling properties of ZM. The main body of work investigated the cause of the observed ZM morphological changes and application of other techniques to control and influence ZM morphology. This project was aimed at providing an in-depth review of zirconium molybdate, a non-heat generating solid known to form in large quantities in HALES and one which has been implicated in many current plant difficulties and future plant operations.

1.4 ZIRCONIUM MOLYBDATE

ZM or giving it its full name zirconium molybdate oxide hydroxyl hydrate, ZrMo$_2$O$_7$(OH)$_2$.2H$_2$O, possesses a body-centred tetragonal unit cell with a 14$_1$cd space group and $a/b = 11.45$ c $= 12.54$ Å (±0.01) at 25°C. The crystal structure is built up from zirconium pentagonal bipyramids (ZrO$_5$(OH)$_2$) linked axially via oxygen bridges to a corner to two distorted molybdenum octahedra (MoO$_4$(OH)(H$_2$O)) and the ZrO$_5$(OH)$_2$ are also linked equatorially to four molybdate octahedra corner linked to
two, and edge linked to the remaining two molybdate octahedra. M-O bond angles, distances, and atomic co-ordination numbers are all within regular parameters, with the exception of one oxygen, which forms a three-way Zr + 2 x Mo bridge (Figure 1.4 and 1.5).

Initial research into ZM centred on its properties as an ion exchange material. The crystalline structure of ZM was first resolved by Clearfield during research into the structure of ion exchange materials in 1969, it was then refined and further analysed in 1972. In 1984 zirconium molybdate found use as a convenient and effective generator of technetium-99m, which was used medically as a radiopharmacological agent for the imaging of organs and tumours. In this technique irradiated Mo was used to produce TcO₄⁻ as an alternative to the conventional fission based Mo generator which also created other fission products providing the technique with many associated problems. ZM gels were used because they have a high molybdenum content and a porous nature which gave the material its good ion exchange properties and allowed TcO₄⁻ to diffuse out of the gel.
Figure 1.4 Diagram showing the arrangement of atoms in zirconium molybdate. (Left) A representation of the organization of the atoms and their interatomic bonds. (Right) A polyhedral representation of the same atomic configuration. Zirconium atoms / units are coloured RED, Molybdenum atoms / units are coloured GREEN, and oxygen atoms are coloured BLUE.

Figure 1.5 Diagram showing the extended zirconium molybdate crystal structure, where $\text{ZrO}_7$ pentagonal-bipyramidal (Red) and $\text{MoO}_6$ octahedral (Green) units are linked in a chain-like structure along the [001] axis and repeating structure in the [100] / [010] axis directions.
1.4.1 *Zirconium Molybdate in HAL*

The presence of zirconium and molybdate solids in nuclear waste reprocessing was first identified during a study by Campbell in 1976.\textsuperscript{34} Kubota then investigated the influence of solids on the stability of high-level waste over long time periods using simulated HAL.\textsuperscript{35} The study placed emphasis on the formation of zirconium and molybdenum containing solids because Campbell had previously identified them as a major product. Kubota found that the concentration of zirconium and molybdenum in the simulant had effects on the final product, as did the concentration of tellurium. Results revealed that the presence of tellurium greatly affected the precipitation of zirconium and molybdenum containing solids, although ZM was not specifically mentioned. Rao carried out further characterization of solids formed in nitric acid solutions (3 molar) containing zirconium and molybdenum which had been treated the same as HLW during reprocessing. The results identified ZM as a product for the first time except when molybdenum was at great excess.\textsuperscript{36} Kondo then published extensive work in 1997 on the formation and filtration characteristics of a number of solids formed in HLW.\textsuperscript{37} He identified the period post-evaporation as the stage in the reprocessing cycle where the majority of ZM precipitated from solution and linked tellurium with the formation of zirconium tellurate.

Doucet was the first to specifically study the step-by-step formation of ZM on substrate surfaces in acidic solutions, with an emphasis on the problems ZM had been known to contribute to during HLW reprocessing.\textsuperscript{38} The results concluded that precipitation began with formation of a thin amorphous film on the surface of the substrate composed of zirconium : molybdenum at a ratio of 1 : 1. Small oval shaped crystals of ZM were then observed to form in the film on the substrate surface, which grew to around 1\(\mu\)m before disappearing and being replaced by larger ZM crystals with
cuboidal morphology. The quantity of ZM crystals was then seen to increase until the surface of the substrate was covered by an interlocking carpet of cuboidal ZM crystals. A sigmoidal curve of precipitated mass over time was presented, which suggested that ZM nucleation was a surface based process and not colloidal.

Two different growth rates were seen when Magnaldo measured the ZM growth kinetics in a system which mimicked HLW processing. The slow initial rate of growth was shown to be caused by slow nucleation. However, once nucleation had occurred a faster growth rate was observed and assigned to fast secondary growth occurring on the surface of the existing ZM deposits. The supersaturation ratio of the reagents and their relationship with nucleation and secondary growth rates were also established for ZM growth using that system.

In all of the articles cited above, ZM is formed directly, using either the sol-gel method set out by Clearfield or from other sources of molybdenum, such as molybdenum metal in the case of HLW studies. However, none of the techniques accurately mimicked the molybdate species produced by CPM which are known to be that major source of molybdenum in post-evaporator HAL, where the majority of ZM forms during HALES processes. The use of phosphomolybdic acid, the major constituent of CPM, had previously been advised for use as the molybdenum source for HAL simulant production. However, in most published work and industrial reports on the formation of solids in HLW simulants, molybdenum metal continues to be used.
1.4.2 CONVERSION OF CPM TO ZM

Over 90% of molybdenum in HAL immediately post-evaporation and prior to ZM formation is present as caesium phosphomolybdate (CPM), Cs$_3$PMo$_{12}$O$_{40}$·14H$_2$O the remainder is possibly ZM.\textsuperscript{15} The CPM structure contains a 12 x MoO$_3$ Keggin cage with a tetrahedral phosphate group at its centre and three caesium counter cations surrounding the molybdate cage (Figure 1.6). In HAL, ZM formation begins when the acidity of the HAL is comparatively low post-WAR and CPM is able to breakdown releasing molybdates into solution.\textsuperscript{15} The freed molybdates then combines with the zirconyl species already present in solution to produce ZM.

![Figure 1.6 Schematics of caesium phosphomolybdate (CPM). (Left) The arrangement of the atoms in the central 12 x Mo Keggin cage with molybdenum atoms coloured purple, oxygen atoms coloured red, and phosphorus coloured orange. (Right) The same structure represented as polyhedral MoO$_6$ octahedra (GREEN) surrounding a central phosphorus (YELLOW).](image-url)
CPM was first associated with the formation of ZM when a study of aged simulant HLW was examined after being left for 8 months at 60°C with slight agitation. The expected dominant golden-yellow colour associated with CPM solids was not present and had been replaced by a dull, off-white solid which was later identified as ZM.

In HALES, CPM forms very quickly during the early stages of HLW reprocessing. Formation of ZM is thought to start soon after irradiated fuel dissolution but the rapid formation of CPM removes the majority of the molybdate from solution preventing further ZM formation. The CPM then slowly begins to breakdown, releasing small amounts of molybdates into solution until the volume reduction stage of HALES reprocessing. Concentration of the waste stream during the volume reduction process increases the acidity of the bulk, something which hinders further breakdown of CPM. Therefore, high acidity stops the formation of ZM until the WAR process reduces the nitric acid concentration of HAL.
1.5 **Crystal Morphology Control**

Classically methods of crystal habit control involve making changes to the crystallization vessel, modifying the rate of crystallization, introducing additives, changing the solvent, altering the degree of supersaturation, adjusting the reagent ratio, changing the pH, or adding polymers or surfactants. Some examples of these methods include increasing the rate of crystallization by the sudden seeding of a supersaturated solution. The introduction of additives or impurities can cause changes to the face specific growth rates of crystals via increased roughness or blocking.

There are however, restrictions to the morphology influencing methods available for use on HALES systems. The options are limited because the crystallization environment and general procedures which are already in place cannot be changed. This limited the techniques available for altering crystal morphology to those which were chemically controlled. However, there are many chemical concentration constraints set by HAL management designed to control other aspects of HAL chemistry or aid downstream HAL processing operations. These constraints limit the presence and concentration of large numbers of chemical species already in HAL and others which are not, further limiting the available possibilities.
1.5.1 **INORGANIC ADDITIVES**

The exact quantities of many of the different molecules, elements, and isotopes in HAL are unknown. It was mentioned previously (Section 1.3) that typically cuboidal ZM crystals had been found with wheat-sheaf morphology in an aged HAL simulant batch. Therefore, one or more of the species present in simulant HAL was responsible for the alteration of ZM morphology. It should be noted that all of the components of HAL and simulant HAL are inorganic with the exception of small quantities of TBP and its related species leftover from the PUREX process. Simulant HAL contains many of the more common elements thought to be present in HAL (Table 1-1) and identification of the chemical(s) which caused the change in ZM morphology could be used to provide control and tailoring of the product’s physical properties. The ability to form ZM crystal with wheat-sheaf or any other morphology has the potential to provide the required alteration to the suspension and settling characteristics of ZM and decrease the problems associated with HAL solids. Utilizing a habit modifying species or set of species already present in HAL would also make the use of a potential additive more acceptable to the chemical concentration constraints in place for HALES.
<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Element</th>
<th>Chemical Used In Simulant</th>
<th>Concentration (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Li</td>
<td>LiNO₃</td>
<td>0.0000</td>
</tr>
<tr>
<td>7</td>
<td>N</td>
<td>NH₄NO₃</td>
<td>1.2493</td>
</tr>
<tr>
<td>12</td>
<td>Mg</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>0.0000</td>
</tr>
<tr>
<td>13</td>
<td>Al</td>
<td>Al(NO₃)₃·9H₂O</td>
<td>0.0239</td>
</tr>
<tr>
<td>15</td>
<td>P (Inorganic)</td>
<td>H₃PO₄</td>
<td>0.0284</td>
</tr>
<tr>
<td>15</td>
<td>P (Organic)</td>
<td>PO(OC₄H₉)₂(OH)</td>
<td>0.0032</td>
</tr>
<tr>
<td>24</td>
<td>Cr</td>
<td>Cr(NO₃)₃·9H₂O</td>
<td>0.0513</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>Fe(NO₃)₃·9H₂O</td>
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</tr>
<tr>
<td>28</td>
<td>Ni</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td>0.0346</td>
</tr>
<tr>
<td>37</td>
<td>Rb</td>
<td>RbNO₃</td>
<td>0.0337</td>
</tr>
<tr>
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</tr>
<tr>
<td>39</td>
<td>Y</td>
<td>Y(NO₃)₃·6H₂O</td>
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</tr>
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<td>40</td>
<td>Zr</td>
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<tr>
<td>42</td>
<td>Mo</td>
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<tr>
<td>43</td>
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<td>44</td>
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<td>46</td>
<td>Pd</td>
<td>Pd solution</td>
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<tr>
<td>52</td>
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<tr>
<td>56</td>
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<td>64</td>
<td>Gd</td>
<td>Gd(NO₃)₃·5H₂O</td>
<td>0.1272</td>
</tr>
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</table>

Table 1-1 Table of the more abundant elements present in HAL, their respective concentrations and the chemical used in the preparation of HAL simulants
1.5.2 **ORGANIC ADDITIVES**

Organic molecules have traditionally been employed as the method of choice for additive induced crystal habit control.\textsuperscript{56} The use of organic additives provides a larger range of possible additives and effects than inorganic addition because there are a potentially large variation in stereochemistry and arrangements of the functional group(s) in an organic molecule allowing the additive to be tailored to suit a particular requirement.\textsuperscript{57-59} The chemistry of the functional group(s) in an organic molecule and the distance between them can be changed to alter the effect and the subsequent outcome in many cases.\textsuperscript{60-62}

A combination of ionizing radiation bombardment and the extremely acidic nature of HAL makes some of the weaker interatomic bonds in organic molecules liable to be broken. Typically the breakdown of organic molecules in these conditions produces a mixture of water, hydrogen, oxygen, and carbon trioxide / dioxide and monoxide gases.\textsuperscript{63} Any release of gases in HAL has the potential to produce foam, the excessive formation of which could carry radioactive material from HAL through pressure releases and other openings into unshielded areas causing significant safety hazards. Therefore, foam production is tightly controlled in HALES and the use of an additive which has the potential to produce foam would not be acceptable. For these reasons, organic crystal habit modifying additives were initially not included in the list of potential additives. However, a possible application for organic additives has since been identified during the post-operative clear-out (POCO) of HALES infrastructure. In the course of POCO all of the HAL solids which cannot be removed by standard processes and which remain in the various HALES vessels will have to be removed. Current thinking is that they will be dissolved using specialized alkaline dissolution agents and then re-acidified in specialized vessels before they are indefinitely immobilized by
vitrification. During re-acidification HAL solids will reprecipitate and it has been thought possible to use organic additives at this stage to influence the growth of these newly forming crystals. It is estimated that several hundred kilograms of CPM and ZM will remain in HALES infrastructure for POCO along with a significant amount of other HAL solids. The large mass of solids would make the suspension properties of the reprecipitated solids important. The re-acidification is expected to produce large quantities of foam and due to the danger of foam production specialized vessels designed to cope would be required. Therefore, the addition of organic molecules would not be expected to provide any additional problems because any foam produced will be contained.
1.6 REFERENCES

5. O'Riordan, T., Rationality and ritual - the Windscale inquiry and nuclear decisions in Britain. Social Studies of Science 1983, 13, (4), 621.
11. NIREX, Facts on NIREX - Disposal of nuclear waste.


51. Boistelle, R.; Simon, B., Epitaxial growth of CdCl₂·2NaCl·3H₂O on the (100), (110), and (111) faces of NaCl. Journal of Crystal Growth 1974, 26, 140.


2 ZIRCONIUM MOLYBDATE SYNTHESIS

2.1 MATERIALS

All materials used were of analytical grade and used without subsequent purification.

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>COMMON NAME</th>
<th>MOLECULAR FORMULA</th>
<th>MOLECULAR WEIGHT (g mol⁻¹)</th>
<th>SUPPLIER</th>
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<tbody>
<tr>
<td>Silicon dioxide</td>
<td>Silica</td>
<td>SiO₂</td>
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<td>84.99</td>
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<td>Potassium Nitrate</td>
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<td>KNO₃</td>
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<td>Tellurium Dioxide</td>
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<tr>
<td>Copper Nitrate</td>
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<td>CsNO₃</td>
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<td>Orthotelluric acid</td>
<td>Telluric acid</td>
<td>Te(OH)₆</td>
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<td>230.43</td>
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<td>Zirconyl Nitrate</td>
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<td>Cobalt Nitrate</td>
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<td>Vendor</td>
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<td>----------------------------------------------</td>
<td>---------------</td>
<td>------------------</td>
<td>-----------------</td>
<td></td>
</tr>
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<td>(2S,3R,4R,5R)-Hexane-1,2,3,4,5,6-Hexol</td>
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</table>

44
2.2 CHARACTERIZATION TECHNIQUES

2.2.1 SCANNING ELECTRON MICROSCOPY (SEM)

SEM was used to provide morphological information on the microcrystalline product samples. SEM analysis was carried out using a JEOL JSM 6330 Field Emission Gun (FEG) scanning electron microscope. Samples were mounted on carbon sticky pads attached to 10mm diameter aluminium stubs and were coated with a 15nm Pt/Pd or Au conductive layer using an Agar High Resolution Sputter Coater. Carbon sticky pads and aluminium stubs were purchased from Agar Scientific.

2.2.2 TRANSMISSION ELECTRON MICROSCOPY (TEM)

TEM was performed in order to image samples in the nanometre size range and to obtain morphological and structural information. TEM analysis was performed in bright field mode using a JEOL JEM 1200 EX TEM operating at 120 kV which was operated with a tungsten filament. Images were captured using a KODAK Electron Image Film SO-163 or a MegaViewII digital camera. Samples were deposited onto 3mm diameter carbon-coated 400-mesh copper TEM grids purchased from Agar Scientific.

2.2.3 SELECTED AREA ELECTRON DIFFRACTION (SAED)

SAED was used in conjunction with TEM and SEM to determine the crystallinity, crystal structure, and orientation of a sample. Diffraction patterns obtained were used to calculate the d-spacing of samples using the formula:

\[ d = \frac{2\lambda L}{D} \]
Where $\lambda$ is the relativistic wavelength of the electron beam, which is equal to 0.334 Å at 120 kV. L is the camera length in millimetres, typically 100mm. D is the distance in millimetres between the diffraction spots and $d$ is the d-spacing or distance between the crystallographic planes responsible for the diffraction pattern.

### 2.2.4 **Energy Dispersive X-ray Analysis (EDXA)**

EDXA was used to obtain qualitative and semi-quantitative elemental information of materials examined under scanning and transmission electron microscopy. The microscopes were fitted with OXFORD INSTRUMENTS ISIS 300 Electron Dispersive X-ray Analysis (EDXA) with an Atmospheric Thin Window (ATW) for light element detection.

### 2.2.5 **Powder X-ray Diffraction (PXRD)**

PXRD was carried out to determine the bulk crystallinity and to identify the crystals present in a sample. It was also used to provide evidence of preferential orientation and changes to lattice parameters. Samples were dried and ground to a powder, if necessary, before being mounted on plastic sample holders. PXRD measurements were taken using a BRUKER D8 Powder Diffractometer with a Cu-K\(\alpha\) radiation source over a scan range of 5 – 60° (2θ), with a step size of 0.0013° 2θ and a dwell time of 0.16 seconds per step. The corresponding interplanar d-spacing of the obtained peaks were calculated using the Bragg equation, where $n$ is the diffraction order and $\lambda$ is the Cu-K\(\alpha\) wavelength (1.5418 Å).

$$d = \frac{n\lambda}{2 \sin \theta}$$
2.2.6 **X-ray Photoelectron Spectroscopy (XPS)**

XPS was used to analyse the elemental composition and electronic state of the surface of a sample with 1 – 5 nm surface penetration. XPS measurements were taken using a VG Scientific ESCAscope spectrometer of dried powdered samples attached to carbon sticky pads (15 mm diameter). Samples were run for 3 hours and the results had an accuracy of 0.1% elemental abundance.

2.2.7 **Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)**

ICP-OES is a technique used to provide quantitative elemental composition analysis of metal ions in solution. ICP-OES measurements were taken using a Varian inductively coupled plasma optical emission spectrometer fitted with a Sturmann master spray chamber and V-Groove nebuliser. Samples were handled using a SPS-5 autosampler and measurements were taken over 50 seconds with 20 seconds stabilization time. Calibrations were made with five samples over a concentration range which encompassed the expected range of concentrations. Samples were prepared by extracting an aliquot of the reaction suspension, diluting the sample to stop any further reaction occurring and then filtering out all solids using a Millipore syringe filter (0.45 μm) and diluting the sample 20 times.

2.2.8 **Settled Bed Stability**

The force required to cause a stable settled bed of solids to change from behaving like an elastic solid and undergo viscose flow was used to measure the force required to re-suspend a settled bed. The samples used were kept in their mother liquors and allowed to settle to a stable volume before use to prevent sedimentation during the experiment. Viscometric measurements of the samples were taken using a rotational
Bohlin CVO Rheometer set to increase the applied shearing force and C25 - V25 cup and vane geometries. Measurements were taken over the shear force range which increased from 0.0123 Pa to 15 Pa over a time of 20 minutes and at a temperature of 25°C. Viscosity measurements were made every two seconds and were analysed using Malvern software.

2.2.9 **SUSPENSION SETTLING**

Settling of suspensions of morphologically altered zirconium molybdate was undertaken to measure the differences in settling time of a set volume fraction of solid sample in suspension. Suspension tests were undertaken using 7 %, 12 %, and 24 % solid suspensions which had been homogeneously suspended in mother liquor. The settled bed volume was then measured constantly until it stabilized at a minimum volume and the results were plotted against time to identify trends.

2.2.10 **SETTLED BED DENSITY**

The density of the settled beds were measured by removing all supernatant from the fully settled product of the suspension settling experiments and then measuring the volume of the sample. All remaining liquid was then removed from the samples by slowly drying in an oven. The weight of the remaining solids were then measured and divided by the volume of the settled bed to give a mass and density measurement.
2.3 Experimental Methods

2.3.1 Preparation of Caesium Phosphomolybdate (CPM)

A solution of caesium nitrate (0.6 M) in nitric acid (2.0 M) was added to a phosphomolybdic acid (0.2 M) in nitric acid (2.0 M) solution with stirring. The product precipitates instantly, and was separated using centrifugation before being washed several times with water and then dried in air at 65°C.

2.3.2 Conditioning of Zirconyl Nitrate Solution

Zirconyl nitrate solution (0.1 M) was added to nitric acid (6 M) and was then heated to 95°C with stirring. The zirconyl nitrate solid dissolved to give a milky-white polymeric solution, which subsequently broke down causing the solution to become clear after 60 minutes. The “conditioned” solution was then allowed to cool to room temperature.

2.3.3 Preparation of Zirconium Molybdate

Caesium phosphomolybdate (CPM), (0.0167 M) was suspended in water (50 mL), to give a working molybdenum concentration of 0.2 M. Conditioned zirconyl nitrate in nitric acid (6.0 M) solution (0.1 M) (50 mL) was then added slowly to the suspension, with constant stirring, to give final concentrations of zirconium = 0.05 M, molybdenum = 0.1 M and nitric acid = 3.0 M. These concentrations reflected those found in HALES plant processes. The mixture was then heated to 95°C under reflux with constant stirring, and was left for typically 3 days but in some cases up to 14 days. The product suspension was then allowed to cool to room temperature before the solid
was separated using centrifugation. It was then washed several times with water before being dried in air at 65°C.

2.3.4 Preparation of Zirconium Molybdate in the Presence of Additives

Inorganic and organic molecules were added to the typical zirconium molybdate synthesis (Section 2.3.3) to investigate their effect on crystallization. This was carried out by introducing the additives to a CPM and conditioned zirconyl nitrate mixture before the reaction was heated.

2.3.5 Scale-Up of Zirconium Molybdate Synthesis

During the scale-up of the zirconium molybdate synthesis the reactants used were the same as during the typical preparation (Section 2.3.3), with or without additive species. A three-necked, 2 litre round-bottomed flask was used as the reaction vessel along with an IKA Eurostar digital overhead stirrer motor and PTFE centrifugal shaft stirrer blade (100 rpm). The round-bottomed flask was filled with up to 2 litres of reactants, as required, and the solution was heated to 95°C using a Thermo Scientific Electrothermal heating mantle. A water-cooled condenser was used and a temperature probe was inserted into the reaction mixture to measure the reactant temperature. The reaction was run for one week before being left to cool to room temperature and the product was isolated and left to settle in the mother liquor.

2.3.6 The Seeding of Zirconium Molybdate Synthesis

Crystals of zirconium molybdate with different morphologies were employed as seed material during further zirconium molybdate synthesis. Seed crystals were produced in batches as required for the specific experiment (Section 2.3.3, 2.3.4 or 2.3.5). The seed crystals were then washed with water several times before being briefly
washed with ammonium carbamate (0.1 M) to remove any remaining caesium phosphomolybdate. The seed material was again washed with water before being dried. The seed crystals were added to the zirconium molybdate synthesis alongside caesium phosphomolybdate and before the addition of the zirconyl nitrate solution. The products of the experiments were then washed, and dried as in typical ZM syntheses.

2.3.7 **The Seeding of Zirconium Molybdate in the Presence of Additives**

Additives known to effect zirconium molybdate crystal morphology were added to a seeded synthesis (Section 2.3.6) to assess the effect on the product. The additives were added to the reaction mixture before the addition of the conditioned zirconyl nitrate solution. The products of the experiments were then washed, and dried as in typical ZM syntheses.
CHAPTER 3

ZIRCONIUM MOLYBDATE SYNTHESIS
3 ZIRCONIUM MOLYBDATE SYNTHESIS

3.1 INTRODUCTION

During the reprocessing of high-level nuclear waste at Sellafield several solids precipitate from the mixture. After separation of uranium and plutonium from the remaining fission products it is necessary to reduce the volume of the waste stream, termed highly active (HA) raffinate at the highly-active liquor evaporation and storage (HALES) building. A significant part of HALES processing is the volume reduction of HA raffinate in evaporators which concentrates the mixture and causes the precipitation of a number of solids. Some of the solids which form during volume reduction are barium nitrate, strontium nitrate and caesium phosphomolybdate. The precipitation of these and other solids creates challenges relating to the management of HALES infrastructure and the transfer of the post-evaporator liquor, now called highly active liquor (HAL), including increased corrosion rates. It is therefore important to understand the mechanisms by which these and other solids form, as well as their properties such as size, shape, solubility, and the effect of temperature or pH.

HAL is at its most concentrated immediately post-volume reduction and therefore, at its most acidic with the nitric acid concentration of HAL reaching a maximum around 12 molar. The HAL is then subjected to a process called water acid reduction (WAR), during which the acidity is reduced to between 2 – 4 molar allowing some of the nitrate solids to re-dissolved. When WAR reduces the acidity of HAL it causes the dissolution of caesium phosphomolybdate (CPM) to begin. CPM is a crystalline solid which contains the majority of molybdenum present in HAL. It is at this point that the majority of zirconium molybdate (ZM) a crystalline solid begins to form. ZM is one of the most abundant solids in post-WAR HAL therefore,
understanding the formation of ZM formation adds to the higher than expected corrosion rates recorded for HAL vessels through the formation of long-lived settled beds of solids in HAL.\(^5\)

Previously all published reports on discrete ZM formation are based on a sol-gel reaction first published by Clearfield in 1972.\(^7\) This method involved the mixing of aqueous solutions of zirconyl chloride (0.5 M) and sodium molybdate (1.0 M) to form a zirconium molybdate gel, which itself has found use as an ion exchange material.\(^7,8\) The gel was then acidified causing it to dissolve and form a colourless liquid, which when heated at reflux temperatures for 24 hours produces ZM. However, the Clearfield method does not reflect the conditions or processes applicable to HALES systems and produced ZM crystals that were often intergrown and multiply-twinned (Figure 3.1). Over 90\% of molybdates in HAL immediately after volume reduction are locked up in CPM and their release upon CPM breakdown initiates ZM formation. Therefore, researchers at Sellafield have developed a method which mimics both the zirconium and molybdenum reagents found in actual HAL and which produces ZM comparable to that found in HALES (Section 2.3.3) (Figure 3.2). The process involved the use of CPM as the molybdate source (Section 2.3.1) and the conditioning of the zirconium reagent by means of the boiling of zirconyl(IV) nitrate in nitric acid (6 M) which replicates the treatment of HAL in HALES and breaks any polymeric character of the zirconyl (Section 2.3.2). Synthesis of ZM using this method has not previously been reported in freely accessible literature and it should be considered a key synthesis due to the special industrial application it possesses.
Figure 3.1 SEM micrographs show samples of ZM formed using the Clearfield method showing (Left) stacked and (Right) intergrown crystals.

Figure 3.2 SEM micrographs shows an example of ZM crystals synthesised in HAL conditions.\textsuperscript{66}
3.1.1 THE CHEMISTRY OF ZIRCONIUM IN ZM SYNTHESIS

The conditioning of the zirconium(IV) reagent is an important process to breakdown the polymeric character present in acidic solutions containing zirconium. A range of molecules and polymers form in zirconium containing solutions and are in part due to the high electrostatic character in bonding of Zr\(^{4+}\) and the small energy gap between low and high coordination numbers.\(^9\) Solvated zirconium(IV) ions, \((\text{Zr}(\text{H}_2\text{O})_8)^{4+}\) are only stable in solution under very acidic conditions and also only at very dilute concentrations (10\(^{-4}\) M) can mononuclear hydroxide complexes be found in any number. At lower acidities the \(\text{Zr}^{4+}\cdot8\text{H}_2\text{O}\) hydrated ion hydrolyses producing a polymeric species connected by hydroxyl and oxygen bridges. When the concentration of zirconium is above 10\(^{-4}\) M the formation of \([\text{Zr(OH)}\cdot7\text{H}_2\text{O}]^{3+}\) occurs. A condensation reaction leads to the formation of \([\text{Zr}_4(\text{OH})_8\cdot16\text{H}_2\text{O}]^{8+}\), a square tetramer which contains four zirconium dodecahedra sharing edges.\(^10,11\) The same square tetramer structure is present in a number of zirconium species including the commonly used reagent zirconyl chloride however, structure determination by X-ray diffraction and density calculations have changed the traditional \(\text{ZrOCl}_2\cdot8\text{H}_2\text{O}\) arrangement to the more accurate \([\text{Zr}_4(\text{OH})_8\cdot16(\text{H}_2\text{O})]\cdot\text{8Cl}^-\) placing the chlorine ions next to each hydroxyl oxygen bridge.\(^12\) The structure of the zirconium tetramer was further refined by Mak using single crystal XRD, Aberg using O-17 and H-1 NMR and a computational study by Rao.\(^13-15\)

The domination of the tetramer in many zirconyl molecular structures was questioned by Tribalat who measured ion concentrations at a range of pH values and concluded that the polynuclear species present at high acidities should be a trimer although this theory came from analysis of data and not through direct observations.\(^16\) The inference of structure without direct observation also occurred when pentamers and
hexamers were suggested to occur in solution when two peaks were identified in a Raman spectra for acidic zirconium solutions, thought to be caused by polymers larger than a tetramer. Support for this theory came from X-ray scattering which proved the existence of octamers, $\text{Zr}_8(\text{OH})_{20}(\text{H}_2\text{O})_{24}\text{Cl}_{12}$, formed from the stacking of two tetramers on top of each other. \cite{18} Singhal demonstrated that the tetrameric and octameric solution species exist in an equilibrium dependent on the acid concentration. For 0.05 M zirconium solutions where $[\text{H}^+] \leq 0.05 \text{ M}$ the prevalent species were octamers, whilst when $[\text{H}^+] \geq 0.6 \text{ M}$ tetramers were seen to dominate. Structurally similar square-planer configurations were found to exist in zirconium oxychloride / oxynitrate and sulphate complexes when formed in aqueous solutions.\cite{19}

Zirconyl tetramers are very kinetically stable such that they can be left in boiling perchloric acid for weeks without being protonated.\cite{14} However, an NMR study revealed that in nitric acid solutions ($> 4 \text{ M}$) one of the bound waters and chlorine ligands was exchanged for nitrates. This causes the breakdown of zirconyl tetramers polymerisation leading to the formation of $\text{ZrO(NO}_3)_2$. Therefore, although zirconyl tetramers are widespread in zirconyl solution chemistry they are not expected to exist in HALES liquor due to the high temperatures and highly concentrated nitric acid used as solvent. Zirconium is expected to exist as $\text{Zr}^{4+}$ probably bound as a nitrate, $\text{ZrO(NO}_3)_2$. 

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3.1.2 The Chemistry of Molybdenum in ZM Synthesis

The breakdown of CPM, Cs₃PMo₁₂O₄₀·14H₂O is an important step in the synthesis of ZM. When CPM crystals are subjected to high temperatures and agitation in a weakly acidic solution they breakdown, releasing their component parts into solution.⁶ The breakdown liberates molybdates into solution, which subsequently react with the already present ZrO(NO₃)₂ causing formation of ZM. The mechanism of CPM breakdown and the subsequent formation of ZM is not well understood and there remains uncertainty about the identity of the intermediate molybdate species. When CPM breaks down the first process expected to occur is the solubilisation of CPM via removal of the Cs⁺ counter cations, leaving phosphomolybdate, [PMo₁₂O₄₀]³⁻ a soluble molecule. The next development was expected to be the thermal decomposition of the PMA into phosphoric acid and molybdate species but the identity of the free molybdate has not been directly characterized in HAL.

A Raman investigation has revealed that two molybdate species, are present in nitric acid after the addition of phosphomolybdic acid (PMA) H₃PMo₁₂O₄₀, these were phosphomolybdate, PMo₁₂O₄₀³⁻ and to a slightly lesser extent oxomolybdate, Mo₂O₅²⁺.²⁰ Oxomolybdate was also identified as the predominant molybdate species in strong hydrochloric acid solutions and 2 - 6 M nitric acid through the use of Mo⁵⁵ / O¹⁷ NMR, making it likely that Mo₂O₅²⁺ is the intermediated molybdate in ZM synthesis.²¹,²² Bond angles and bond lengths of Mo₂O₅²⁺ have been measured in highly acidic solution using EXAFS and XANES showing that oxomolybdate consists of two MoO₂²⁺ centres linked by a bridging oxygen (Figure 3.3).²³,²⁴ Further weight was added to the viability of Mo₂O₅²⁺ as an intermediate during ZM synthesis because it can be directly transposed into the structure of ZM, providing a link between the reagent and the product (Figure 3.4).
Figure 3.3 Structure of $\text{M}_2\text{O}_5^{2+}$ known to exist in nitric acid and thought to be the intermediate molybdate species in ZM synthesis.

Figure 3.4 Part structure of ZM showing the presence of the oxomolybdate, Mo$_2$O$_5^{2+}$ species present in solution.

Equation 3.1 - $\text{Cs}_3\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O} + 3\text{HNO}_3 \rightleftharpoons \text{H}_3\text{PMo}_{12}\text{O}_{40}^{3-} + 3\text{CsNO}_3$

$$\text{H}_3\text{PMo}_{12}\text{O}_{40}^{3-} + 12\text{H}^+ \rightleftharpoons 6\text{Mo}_2\text{O}_5^{2+} + \text{H}_3\text{PO}_4 + 6\text{H}_2\text{O}$$

$$\text{Mo}_2\text{O}_5^{2+} + \text{ZrO(NO}_3)_2 + 5\text{H}_2\text{O} \rightarrow \text{ZrMo}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O} + 2\text{HNO}_3 + 2\text{H}^+$$

Overall - $\text{Cs}_3(\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O} + 6\text{ZrO(NO}_3)_2 + 10\text{H}_2\text{O} \rightarrow$

$$6[\text{ZrMo}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O} + \text{H}_3\text{PO}_4 + 3\text{CsNO}_3 + 9\text{H}_2\text{O}$$
The 12 molybdenum centres in CPM exist in a polyoxometalates (POM) structure. There are eleven different POM cluster structures with sizes ranging from 36 metals centres in polymolybdate to five in a Strandberg cluster. Three of the most commonly experienced POM structures are Anderson (XM$_6$O$_{24}$), Keggin (XM$_{12}$O$_{40}$), and Dawson-type (X$_3$M$_{18}$O$_{62}$). Anderson-type POMs are the smallest and includes hexamolybdatellurate. Keggin-type POM structures are the most researched because they are useful catalysts. Dawson-type clusters are formed when a solution containing Keggin-type POMs is left to stand and is made of two Keggin POMs with the top or bottom faces removed and the remaining cages fused together. The ZM reagent CPM [PMo$_{12}$O$_{40}$]$^{3+}$ is a Keggin-type POM with a structure containing a central phosphate tetrahedron surrounded by twelve molybdate octahedra. Keggin-type POM have a cage-like structure which in CPM is made up of molybdates spaced equidistant from the central heteroatom (Figure 3.5).

Figure 3.5 Ball and stick (Left) and Polyhedral (Right) representation of a Keggin POM cluster. Oxygen = Red. Metalate (Molybdenum) = Purple. Heteroatom (Phosphorous) = Orange. Polyhedral representation is comprised of MO$_6$ octahedra and shows cage surrounding the central heteroatom.
There are comparisons to be drawn between the chemistry of complexes formed by different POMs. The majority of Keggin-metal complexes use the lacunary Keggin \([\text{XM}_{11}\text{O}_{38}]^+\) as the ligand unit because the terminal oxygens in the MO₂ vacancy possess increased reactivity over the fully bound Keggin. Lacunary phosphomolybdate Keggin structures, PMo₁₁O₃₀, are not as stable as their tungsten analogues (PW₁₁O₃₀) and therefore there are fewer published structures. Many different structures have been reported for lacunary tungstate POM materials including 2D / 3D extended structures and sandwich complex clusters. Lanthanide-linked lacunary molybdate sandwich complexes have been prepared for the whole lanthanide series (except promethium). However, the higher stability of the lacunary tungstate clusters allows the formation of transition metal sandwich complexes. The sandwich structures have a general formula of \(\text{Ln}^{(III)}(\text{PMo}_{11}\text{O}_{30})_2^{11-}\), but there has been no report of full Keggins bound to lanthanide or transition metal ions making metal-Keggin complex formation in HAL unlikely.

A study of POM structures in solution using \(^{31}\text{P}-\text{NMR}\) reported that Keggin-sandwich complexes were the only POM complexes present in acidic solutions of Zr⁴⁺ at pH 1 - 2. In more neutral conditions the lacunary cluster begins to appear, reaching a maximum concentration at pH = 4.6. Above pH = 4.9 the polyoxomolybdate structure breaks down into molybdic acid and phosphate. However, at pH = 1 the only POM present is PMo₁₂O₄₀ and a zirconium(IV) Keggin sandwich complex is recorded through the pH range 1 – 4.9.
3.2 RESULTS AND DISCUSSION

3.2.1 SYNTHESIS OF ZIRCONIUM MOLYBDATE

Zirconium molybdate (ZM), $\text{ZrMo}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$, was synthesised using the method stated in section 2.3.3. This involved reaction of the microcrystalline caesium phosphomolybdate (CPM), $\text{Cs}_3\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$, with "conditioned" zirconyl nitrate, $\text{ZrO(NO}_3)_2$ in nitric acid (3 M). This method of ZM production was previously formulated to mimic the precipitation of ZM during the course of HAL processing in HALES, Sellafield.1, 7, 43-45 The product of the synthesis was imaged using scanning electron microscopy (SEM) (Figure 3.6), revealing cuboidal crystals. The identity of the product was confirmed using powder X-ray diffraction (PXRD) analysis as ZM with a body-centred tetragonal unit cell (Figure 3.7).46 The space group of ZM is $I4_1cd$ with $\alpha$, $\beta$, $\gamma = 90^\circ$, $a = b = 11.45$ Å and $c = 12.49$ Å. The ZM crystals possessed a flattened-cuboidal form, thought to be shortened along the [001] axis because the [100] and [010] axes are identical. The morphology of the product related well to that of ZM formed during HALES processes.47
Figure 3.6 SEM micrograph of zirconium molybdate (ZM)

Figure 3.7 PXRD pattern of ZM with main Miller indices
3.2.1.1 Elemental Analysis of ZM Synthesis

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the concentration of zirconium and molybdenum metal ions in solution during a typical synthesis of ZM (Section 2.3.3). The analysed samples were taken at a range of reaction times beginning when the reactants were first mixed. It is prudent to note that the measured molybdenum concentration refers to molybdenum in the solution phase, which originates from CPM breakdown and not that which was trapped in the reagent. The molybdenum was then present in solution until it is taken back into the solid phase in the form of ZM. The zirconium reagent was soluble from the start and any concentration decrease was deemed to be due to uptake into ZM.

The ICP-OES measurements taken during the synthesis of ZM revealed a trend for the concentration of molybdenum, [Mo] revealed that early in the reaction it reached a maximum and then dropped to a stable level for the remaining time (Figure 3.8). The [Mo] peak had a maximum of 720 ppm at 2:30 hours, the [Mo] then decreased to around 180 ppm, at which it remained until a time of 55 hours. During the same reaction the concentration of zirconium, [Zr] started high (2900 ppm) and after a brief delay decreased rapidly for 24 hours after which the rate of decrease slowed and approached a base level of 50 ppm at 60 hours.

The peak in the [Mo] trend at 2:30 hours can be explained by considering that during this period ZM crystal growth had yet to begin therefore, all molybdenum released by CPM breakdown was able to build up in solution. In HALES conditions the nucleation of ZM was expected to occur heterogeneously on the vessel surface when [Mo] reaches supersaturation at a concentration = 0.6 g l\(^{-1}\).^{48} This value converts to [Mo] = 600 ppm and therefore, the slightly higher [Mo] peak (720 ppm) is caused by the slow primary nucleation rate of ZM. Once crystal growth has begun surface
nucleation and growth on existing ZM crystal surfaces occurs preferentially in advance of any secondary nucleation. This means that all available molybdenum should be being used in growth on existing ZM crystals when [Mo] is less than the supersaturation value. Therefore, it can be assumed that after five hours, initial heterogeneous nucleation ceases and reagent uptake occurs almost solely as growth on existing ZM crystals.

Figure 3.8 Graph of zirconium, [Zr], and molybdenum, [Mo], concentration in solution over time measured using ICP-OES.
After the [Mo] peak at 2:30 hours, the concentration showed a slow decrease as CPM was being used up. However, towards the end of the reaction, at $t > 55$ hours, the [Mo] trend changed and it began to increase slowly (Figure 3.9). Explanation of this became apparent when it was considered that up to the point at 55 hours the [Zr] was in excess when compared to molybdenum and that the stoichiometric ratio required to produce ZM ($\text{ZrMo}_2\text{O}_7\text{(OH)}_2\cdot2\text{H}_2\text{O}$) is $1:2$ [Zr] : [Mo]. Therefore, before 55 hours [Mo] was the limiting reagent in ZM synthesis because it relied on the slow breakdown of CPM. After 55 hours the finite amount of zirconium, present in solution from the start of the reaction, drops below half that of available molybdenum, making [Zr] the limiting factor. Once this point had been passed the rate of molybdate released into solution exceeded rate of uptake at 55 hours resulting in a slight [Mo] increase.

![Graph of [Zr] and [Mo] measured using ICP-OES.](image)

**Figure 3.9** Graph of [Zr] and [Mo] measured using ICP-OES. Area of graph shown represents the stage where [Zr] becomes less than half [Mo] and [Mo] subsequently begins to increase.
The rate of ZM synthesis was calculated from the [Zr] data acquired from ICP-OES. It was achieved by assuming that all zirconium was present in solution at the start of the reaction (t = 0) and was irreversibly and solely used up during the synthesis of ZM. The reaction was also assumed to be a pseudo first order reaction for the majority of the reaction time because zirconium was in excess. The viability of this assumption was tested by assessing the linear relationship between the natural logarithm of [Zr] with time up to 48 hours (Figure 3.10). The result was an R² value of 0.99 a value that indicated the use of a first order rate equation was valid. Equation 3.2 calculates the concentration of zirconium at any time, and can be used to calculate the rate constant for zirconium uptake, and hence the rate of ZM formation (k[ZM]), using equation 3.3 in which [Zr]₀ is the initial concentration, t is the time in hours and k is the rate constant.

The progress of the ZM formation reaction is the inverse of the decrease of [Zr] and the result was a rate constant for zirconium synthesis, k[ZM] = 0.061 hr⁻¹ over the time of the whole reaction (Figure 3.11). The rate of ZM production reached a maximum between 5 and 24 hours. The sigmoidal nature of the ZM synthesis progress curve is visible in Figure 3.12. The figure shows a short nucleation delay followed by a steady increase in [ZM] during the growth stage and an extended completion time where the final reactants were slowly used up, typical of first order reactions.

Equation 3.2 - \[ [Zr] = [Zr]_0 e^{-kt} \]

Equation 3.3 - \[ k[ZM] = -\frac{d[Zr]}{dt} \]
Figure 3.10 Graph showing the relationship between the natural log of [Zr] and time. The R² value represents a good linear fit for the data and suggests that the decrease of [Zr] can be modelled by a first order rate equation (Equation 3.2).

Figure 3.11 Graph showing the decrease in [Zr] as the reaction progresses and the calculated relative increase in [ZM] as the reactant is consumed and the product is formed. [ZM] is calculated from equation 3.3. The black line represents the calculated exponential progress of the [Zr] decrease during the reaction.
3.2.2 Caesium Phosphomolybdate Breakdown

CPM was synthesised using the method stated in section 2.3.1 and its identity was confirmed using PXRD as a crystal with the cubic space group $Pn3m$ (Figure 3.12).\textsuperscript{46,49} SEM analysis of the product CPM crystals (Figure 3.13) revealed solids that were roughly spherical with no defined edges and which resemble polycrystalline aggregates.

The experiment took place in conditions similar to those experienced during ZM production; CPM crystals (0.0083 M) were placed in nitric acid (3 M) and heated to 95°C, the morphology of CPM crystals during breakdown is shown in Figure 3.16. The SEM micrographs reveal how the initially smooth surface of the CPM crystals became roughened after four hours, followed by the formation of holes after 24 hours. The aggregates were then broken open during the final stages of breakdown revealing a hollow centre (Figure 3.15) however, TEM imaging showed crystals which did not appear hollow (Figure 3.14). These results suggest that the surface of CPM crystals might become covered with a layer of highly crystalline CPM when the breakdown of CPM caused the solution concentration of reagents to increase past their supersaturation point. This would result in secondary CPM nucleation on the surface of the CPM causing the formation of a layer of highly crystalline CPM which would be more resilient to breakdown.\textsuperscript{50}
Figure 3.12 PXRD pattern of caesium phosphomolybdate (CPM). Miller indices of lattice planes responsible for reflections shown in brackets.

Figure 3.13 SEM micrograph of caesium phosphomolybdate (CPM) with close-up inset, scale bar represents 1 μm.
3.2.3 **Substituting Phosphomolybdic Acid for Caesium Phosphomolybdate**

During the in lab synthesis of ZM from CPM, a number of problems were experienced caused by the presence of left-over CPM solids in the final product mix and the length of time required for the reaction to go to completion. These problems were partly a result of the long time required for CPM to breakdown and release molybdenum into the reaction mix. In most cases, the reaction was stopped before it had gone to completion for practical reasons. In these instances, there remained an amount of CPM solid present in the product, causing accurate characterization of ZM to become hampered and confused.
Phosphomolybdic acid (PMA) \([\text{H}_3\text{PMo}_{12}\text{O}_{40}]\) is used in CPM production (Section 2.3.1) and was identified as an intermediate in the breakdown of CPM during ZM synthesis (Section 3.1.2). For these reasons, PMA was chosen to be trialled as a cleaner reagent for the formation of zirconium molybdate, literature provided no evidence that this reaction had been previously attempted. It was thought that the use of PMA would allow ZM synthesis to occur via the same mechanism as CPM containing reaction but with the advantage of PMA being highly soluble in solution whereas CPM is only partly soluble in hot mildly acidic solution.\(^6\) Therefore, removing the problems associated with slow reaction rate and having another solid present in solution. The solid product of this reaction was shown to be ZM only (Figure 3.16). The product was not however, the flattened cuboidal crystals which could have been expected but poorly formed elongated crystals instead (Figure 3.17).

![Figure 3.16 PXRD pattern of ZM synthesis using PMA including Miller indices](image)

**Figure 3.16 PXRD pattern of ZM synthesis using PMA including Miller indices**
3.2.3.1 Optimization of the use of phosphomolybdic acid as a reagent

For the use of PMA as a reagent for clean ZM synthesis to be undertaken on a regular basis the product would be required to better resemble the cuboidal ZM crystals seen in HAL. A number of crystal habit control techniques were tested in attempt to produce cuboidal ZM using PMA as a reagent.

Changing the starting concentration of PMA caused alterations to the product morphology, the results show how the increased availability of molybdates when the concentration of PMA was high induced ZM to grow into a non-equilibrium shape (Figure 3.18). When the initial concentration of PMA was increased, the ZM crystals produced were further elongated and less well formed, resembling a cigar when the concentration of PMA reached 400 molar percent (mol %) with respect to typical CPM.
concentration (Figure 3.18F). Elongation occurred along the [001] axis, as proven by SAED (Figure 3.19). However, decreasing the concentration of PMA caused the product crystals to become increasingly cuboidal and at 6 mol % PMA resembled the cuboidal ZM formed through use of CPM (Figure 3.18A).

An SAED pattern was taken from a representative sample of the elongated crystal product and the diffraction spots were indexed using the crystallographic data described by Clearfield. The presence of the [004], [004] and [200], [200] diffraction spots show that the planes with the (001) and (100) Miller indices are present respectively and that the zone axis of the image was [010]. Assessment of the TEM micrograph and the direction of the lattice planes in the diffraction pattern showed that the elongation occurred along the [001] axis. Comparison of the zone axis of a number of different SAED patterns of ZM crystals have revealed that flat faces of the cuboidal crystals must occur along the [100], [010], and [001] axes.
Figure 3.18 SEM micrographs showing the effect of different PMA concentrations on the product ZM crystals. A – 10 mol % PMA, ZM crystals are most like control ZM, flattened along 001 axis, Aspect ratio = 0.5. B – 25 mol % PMA, ZM crystals are cubic, Aspect ratio = 1. C – 50 mol % PMA, ZM crystals begin to elongate along c-axis, Aspect ratio = 1.2. D – 75 mol % PMA, Aspect ratio = 2. E – 200 mol % PMA, Aspect ratio = 3. F – 400 mol % PMA, Aspect ratio = 5.
The reason for this variation in morphology was thought to be a change to the rate of reaction. Using PMA removed the slow dissolution associated with CPM, allowing the molybdates to be available for synthesis much faster allowing reagent control of ZM synthesis rate. This method allowed ZM to form using an identical molecular mechanism to that which uses CPM, but without the problems associated with having another solid present. However, there were drawbacks of using this method to produce cuboidal crystals, which included a decreased product yield caused by the reduced reactant concentration. For a PMA reaction to produce cuboidal crystals, in an amount similar to that normally attained, the volume of the reaction vessel would have to be increased by fifteen times.

In theory, changing the acidity of the reaction would slow the breakdown of the Keggin structure present in PMA (Equation 3.1) and slow the rate of Mo$_2$O$_5^{2+}$ release into solution. The concentration of Mo$_2$O$_5^{2+}$ in solution controls the rate of reaction and ultimately the morphology of ZM crystals. Therefore, slowing the release of Mo$_2$O$_5^{2+}$ by using a lower acidity solution could have an effect similar to limiting the initial PMA concentration, without affecting the yield. However, when tested, and the acidity was decreased from 3 M to 1 M, the product appeared mostly unaffected (Figure 3.20). Although this result was not directly useful it did provide evidence that the breakdown of PMA in acidic solution was fast and that it would occur throughout the changing acidities of an intricate system such as HALES.
Figure 3.19 TEM image of ZM synthesised using PMA in place of CPM. Right is an SAED pattern showing the axis of elongation of the ZM crystal.

Figure 3.20 SEM micrographs showing the affect of pH on PMA facilitated ZM growth. 
A – pH = 0. B – pH = -0.48
The preference of ZM to grow along the [001] axis can be explained by considering the separate growth mechanisms required in the [100]/[010] axis directions compared to the [001] axis direction (Figures 3.22 and 3.23). The intermediate molecules in the ZM synthesis mechanism proposed in equation 3.1 (Section 3.1.2) were ZrO(NO$_3$)$_2$ and Mo$_2$O$_5^{2+}$. The proposed binding of the intermediates to either the (100)/(010) or the (001) crystal faces or their partner opposites are shown in figures 3.22 and 3.23 respectively. The points of contact are represented as arrows in the figures and the more arrows between units the more corner / edge shared oxygens and the stronger the attachment. In the proposed mechanism when Mo$_2$O$_5^{2+}$ attaches to the (100)/(010) crystal faces there is one attachment point (Figure 3.21A). However, there are three points where Mo$_2$O$_5^{2+}$ attaches to the (001) crystal face. Therefore, the probability of the incoming Mo$_2$O$_5^{2+}$ unit permanently binding to the (001) face was greater than the probability of it permanently attaching to the (100)/(010) face, meaning that during synthesis the (001) face would be populated first. When the growth rate was slow the molybdates had the opportunity to populate all growth sites on the surface of the crystal, allowing formation of an equilibrium structure. If the crystal growth rate was faster the probability was that the Mo$_2$O$_5^{2+}$ would populate the (001) face faster and therefore, the [001] axis would be able to grow faster. This would explain the preference for final crystal product elongation along the [001] axis when the rate of crystal growth was increased.

The Mo$_2$O$_5^{2+}$ unit, used in these mechanisms, was the most prevalent molybdate species in highly acidic solution. The remaining molybdates were probably monomolybdate species possibly MoO$_3$·3H$_2$O octahedra, which would be equally capable of binding to both crystal faces.
Figure 3.21 Attachment of (A) \( \text{Mo}_2\text{O}_5^{2-} \) (Green) and (B) \( \text{Zr}^{4+} \) (Red) to ZM crystal surface. Figures show how units attach during growth to the (100)/(010) crystal faces. The formation of perminant bonds between units and the crystal surface are indicated by a black arrow. Figures describe how units binding to the (100)/(010) ZM crystal faces do so by the formation of a single bond.
Figure 3.22 Attachment of (A) Mo$_2$O$_5^{2-}$ (Green) and (B) Zr$^{4+}$ (Red) to ZM crystal surface. Figures show how units attach during growth to the (001) crystal faces. The formation of permanent bonds between units and the crystal surface are indicated by a black arrow. Figures describe how units binding to the (001) ZM crystal face do so by formation of multiple bonds.
3.3 CONCLUSIONS

Zirconium molybdate was synthesised using a two-step method, which closely resembled the manner of precipitation relevant to nuclear waste reprocessing industry. This process should be preferentially employed over other synthetic methods for accurate production of zirconium molybdate during research into the nuclear reprocessing cycle. The process has been shown to be rate limited by the release of molybdenum from caesium phosphomolybdate, which it is thought undergoes a two-step breakdown process via two intermediates $\text{PMo}_{12}\text{O}_{40}$ and $\text{Mo}_2\text{O}_5^{2+}$. The rate of zirconium molybdate precipitation was calculated under typical conditions and shown to follow a first order rate equation. Caesium phosphomolybdate solids were characterized and shown to breakdown and reveal a hollow shell of recrystallized CPM formed on what appeared to be a nanocrystalline aggregate material. Zirconium molybdate was also created using a simple novel method, which whilst being analogous to the process by which zirconium molybdate is produced industrially, had none of the drawbacks of using CPM. The synthesis involves substitution of caesium phosphomolybdate with phosphomolybdic acid, which is an intermediate in the breakdown of caesium phosphomolybdate. The advantage of this system was the solubility of phosphomolybdic acid, which led to a faster reaction time and increased control over the morphology especially the elongation of the product. The ZM crystal elongation occurred along the [001] axis of the crystal because the number of attachment sites was higher at the (001) crystal face. This allowed stable binding of growth units and in an accelerated growth situation caused faster growth along the direction of the [001] axis.
3.4 References


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34. Ernst, V.; Barbaux, Y.; Courtine, P., Phosphomolybdic acid ($H_3PMo_{12}O_{40}$) as a catalyst for the vapour-phase oxidative dehydrogenation of isobutyric acid: kinetic parameters of supported and unsupported catalysts. Role of water. Catalysis Today 1987, 1, (1-2), 167.

35. Gaunt, A. J.; May, I.; Collison, D.; Fox, O. D., A novel zirconium polyoxometalate complex that contains both a coordinated saturated anion, $PMo_{12}O_{40}^{3-}$, and a coordinated unsaturated anion, $PMo_{11}O_{39}^{2-}$. Inorganic Chemistry 2003, 42, (17), 5049.


38. Gaunt, A. J.; May, I.; Sarsfield, M. J.; Collison, D.; Helliwell, M.; Denniss, I. S., A rare structural characterisation of the phosphomolybdate lacunary anion, PMo$_{11}$O$_{39}$$^{-7}$. Crystal structures of the Ln(III) complexes, (NH$_4$)$_{11}$Ln(PMo$_{11}$O$_{39}$)$_2$ center dot 16H$_2$O (Ln = Ce-III, Sm-III, Dy-III or Lu-III). Dalton Transactions 2003, (13), 2767.


Chapter 4

The Influence of Inorganic HAL Components on

Zirconium Molybdate Crystal Growth
4 THE INFLUENCE OF INORGANIC HAL COMPONENTS ON ZIRCONIUM MOLYBDATE CRYSTAL GROWTH

4.1 INTRODUCTION

Zirconium molybdate (ZM) is known to precipitate from highly active liquor (HAL) along with several of other solids during the reprocessing of irradiated nuclear waste.¹ The solids present in HAL including ZM, are known to cause a number of problems for HALES corrosion management, some of the challenges are described in section 1.3 and are a symptom of the fast settling of the solids from a suspended state. Examination of solids formed in aged HAL simulant, similar to that which would be found in highly active storage tanks (HASTs), revealed the formation of ZM crystals with an unexpected morphology (Figure 4.1).² The reason for this change in crystal morphology was unknown and attributed at the time to the influence of one or more of the chemical components of the simulant HAL in which the ZM crystals were produced. The usually cuboidal crystals instead possessed a wheat-sheaf morphology, typified by crystals with an elongated body, thin centre, and divergent termini. The findings discussed in chapter 3 revealed ZM crystals which became elongated when the rate of formation was increased although a wheat-sheaf morphology was not seen. It was reasoned that crystals with a wheat-sheaf morphology would possess improved suspension and settled bed properties compared to cuboidal ZM and in that way provide improved manageability of the ZM crystals in HAL. If the cause of this morphological alteration could be established it was thought that it could be exploited to allow selective formation of crystals with different and potentially useful morphologies when required. Therefore, investigation into the cause of the observed morphological change was undertaken through the use of an array of different HAL components as additives to discrete ZM syntheses.
HAL is composed mainly of fission products and minor actinides dissolved in nitric acid (Table 4-1). The effects which the constituent elements of HAL have on the growth of any of the solids known to form in HAL are poorly understood. The work in this section was designed to investigate the growth of ZM in the presence of some of the major components of HAL and establish which component(s) caused the formation of the observed crystals with a wheat-sheaf morphology, and if any other qualities were affected. There was also focus on the potential for any altered product crystals to improve the manageability of ZM solids by achieving morphologies favourable to low settling and open-packing.³
<table>
<thead>
<tr>
<th>Atomic Number</th>
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<th>Concentration (mol/l)</th>
</tr>
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</tr>
<tr>
<td>7</td>
<td>N</td>
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</tr>
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<td>12</td>
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<td>15</td>
<td>P (Inorganic)</td>
<td>H₃PO₄</td>
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</tr>
<tr>
<td>15</td>
<td>P (Organic)</td>
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Table 4-1 Table of some the more abundant elements present in HAL, their respective concentrations and the chemical used in the preparation of HAL simulants.
4.2 **RESULTS**

4.2.1 **USING HAL CONSTITUENT ELEMENTS AS ADDITIVES**

Experiments were undertaken to investigate whether any of the chemical species present in HAL could affect the growth of ZM crystals. Due to the complexity and variability of HAL many different chemical species were potentially present during the period of HAL processing where the majority of ZM formation would take place. Which meant that the task of testing the effect of each component species on ZM synthesis would have been too time consuming for this project, due in part to the time required for each ZM synthesis. Instead a large number of the more abundant HAL component species were chosen and tested. HAL contains many radioactive species which for safety reasons were not included in testing, although where possible and required non-radioactive isotopes were used in their place.

The experimental method used during this investigation was described in section 2.3.4. In summary, the experiment was set up using the same method used in chapter 3 for a typical ZM synthesis but a set amount of the chosen additive material was introduced to the mixture immediately after the other reagents. The HAL component chemical species were added independently to discrete ZM syntheses so that their individual effect on ZM crystal synthesis and product morphology could be gauged. The concentration of the additive was set to a standard amount higher than the concentrations of most components in HAL relative to ZM, with the purpose of making any effects on ZM synthesis immediately identifiable. A concentration of 50 molar percent (mol %) with respect to the theoretical final ZM yield was used in all cases during the initial trials. The additives used were nitrate salts where possible, to reflect the likely identity of most species in HAL systems.
Figure 4.2 SEM micrographs of the products of the addition of some HAL components and some commonly available chemicals as additives. Further details of the identity of the additives are presented in Table 4-2.
<table>
<thead>
<tr>
<th>Element</th>
<th>Chemical Used In HAL Simulant</th>
<th>Used As Additive?</th>
<th>Chemical Used As Additive</th>
<th>Effect on ZM?</th>
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<td>Li</td>
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</tr>
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<td>Y</td>
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<td>Pb</td>
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<td>Y</td>
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<table>
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<th>Common Chemicals Used as Additive</th>
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<tr>
<td>NaNO₃</td>
</tr>
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<td>Na₂WO₄</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
</tr>
</tbody>
</table>

Table 4-2 The results of inorganic species additive tests showing the chemicals used and whether they caused a perceivable effect on the product ZM crystals.

Figure 4.3 SEM micrograph of the product of the addition of 50 mol % tellurium dioxide to ZM synthesis. Image shows elongated ZM crystals and flaky tabular material.
Micrographs of the crystalline products of the additive trials are shown in figure 4.2 and the results summarised in table 4-2. The results show that the addition of HAL components as additives did not have an obvious influence on the synthesis of ZM crystals in all but one instance. The products of the introduction of additives in most instances were cuboidal ZM crystals, similar to the control ZM produced in absence of any additives (Section 3.2.1 Figure 3.1). The products were confirmed as ZM in all cases using PXRD, although a small amount of reagent CPM remained in some samples. The only HAL component additive to have an effect was tellurium, the 23rd most abundant element in HAL. The tellurium additive chosen in this first trial was tellurium\(^{IV}\) dioxide (TeO\(_2\)). When introduced to the start of ZM synthesis, the tellurium additive had a distinct effect on the morphology of the crystals produced. The presence of which at 50 mol % caused the production of elongated ZM crystals surrounded by minor amounts of unidentified flaky tabular material previously unseen (Figure 4.3). PXRD identified that the majority of the sample was ZM, and TEM imaging coupled with SAED implied that the flaky tabular material was not crystalline. More detailed investigation of Te\(^{4+}\) and Te\(^{6+}\) additives are given in section 4.2.2.

Some commonly available and selected inorganic additives were also tested using the same method as that employed for HAL components (Table 4-1). From these trials the only additive to have an effect on ZM morphology was sodium tungstate (Na\(_2\)WO\(_4\)). W\(^{6+}\) was chosen because it had similar chemistry to Mo\(^{6+}\) and an ability to substitute for molybdenum in crystal lattices. A process which in one instance producing negative thermal expansion materials.\(^5,8\)
At low concentrations the addition of W⁶⁺ to ZM synthesis caused the formation of ZM crystals containing holes and defects (Figure 4.4). At higher concentrations (50 mol %) W⁶⁺ addition resulted in the production of a zirconium tungstomolybdate gel, a similar preparation to that which was first published by Nabi for use as an ion exchange material.⁹ In summary, the use of W⁶⁺ additives produced no change to the general morphology of the crystals and therefore, would be likely to produce little or no change to the settling properties of ZM crystals. Increased porosity of a solid may cause a slight improvement to settling rates but the formation of a gel has the potential to further stabilize any settled solids. It should also be taken into account when considering this result that W⁶⁺ is not an abundant element in HAL therefore, its effects on all other HAL processes are unknown.

Figure 4.4 SEM micrograph showing the formation of holes and defects in the ZM crystals synthesised in the presence of sodium tungsten additive (0.5 mol %)
4.2.2 TELLURIUM ADDITIVES

In the previous section, it was revealed that Te\textsuperscript{IV} was the only HAL component trialled which exhibited an influence on the growth of ZM crystals. This section examines the effect of changing the tellurium additive concentration and form in attempt to better understand its influence.

4.2.2.1 THE EFFECT OF TELLURIUM\textsuperscript{(IV)} OXIDE AS AN ADDITIVE TO ZM SYNTHESIS

Te\textsuperscript{IV}O\textsubscript{2} is insoluble in water but forms a soluble nitrate salt (Te\textsubscript{2}\textsuperscript{IV}O\textsubscript{4}.HNO\textsubscript{3}) in concentrated nitric acid over time.\textsuperscript{5,10} When trialled at a variety of concentrations the Te\textsuperscript{IV}O\textsubscript{2} additive showed a range of influences. At a concentration of 2 mol % Te\textsuperscript{IV}O\textsubscript{2} had no apparent effect on ZM morphology, which remained cuboidal (Figure 4.5A). When the Te\textsuperscript{IV}O\textsubscript{2} additive concentration was increased to 10 mol % (Figure 4.5B), the product was ZM crystals which were elongated to varying degrees possessing aspect ratios ranging from 1.3 to 4. When the starting concentration of Te\textsuperscript{IV}O\textsubscript{2} was increased to 50 mol % the product ZM crystals possessed an average aspect ratio of 2.3, only slightly greater than that of the crystals produced in the presence of 10 mol % additive. There were also large amounts of flaky tabular material present in this sample which were not present at 10 mol % additive concentration. At additive concentrations greater than 50 mol % the Te\textsuperscript{IV}O\textsubscript{2} additive caused only slight increases to the aspect ratio of the crystals from those previously seen (Table 4-3). At concentrations above 50 mol % Te\textsuperscript{IV}O\textsubscript{2} the flaky tabular material became increasingly abundant and at 100 mol % began to form intergrown tabular arrays (Figure 4.5D) PXRD confirmed there to be very little ZM present. Overall these results show that the use of Te\textsuperscript{IV}O\textsubscript{2} as an additive has the potential to cause moderate elongation of ZM crystals but with the disadvantage of forming a flaky solid material. The increased abundance of the flaky solid at higher Te\textsuperscript{IV}O\textsubscript{2} concentrations suggests that it was a deposited tellurium phase although PXRD could
It was also noted that the wheat-sheaf ZM morphology observed during the characterization of aged HAL simulant solids was also not observed during these trials.

Figure 4.5 SEM micrographs showing the influence of different concentrations of $\text{Te}^{2+} \text{O}_2$ on ZM synthesis. A = 2 mol %  B = 10 mol %  C = 50 mol %  D = 100 mol %
Additive Average Concentration Aspect Ratio

<table>
<thead>
<tr>
<th>Additive Concentration</th>
<th>Average Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mol %</td>
<td>1.1</td>
</tr>
<tr>
<td>2 mol %</td>
<td>1.1</td>
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<td>50 mol %</td>
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</tr>
<tr>
<td>100 mol %</td>
<td>2.7</td>
</tr>
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Table 4-3 Table showing the aspect ratio of ZM crystals produced in differing concentrations of Te$^{IV}$O$_2$ additive

4.2.2.2 The Effect of Tellurium Nitrate As an Additive on ZM Synthesis

It is unlikely that any tellurium present in HAL would have taken the form of an oxide, such as Te$^{IV}$O$_2$, and it is known that the soluble form of Te$^{IV}$O$_2$ in nitric acid is tellurium nitrate Te$_2^{IV}$O$_4$.HN0$_3$. Therefore, to make the use of Te$^{IV}$ more efficient tellurium (IV) nitrate was used directly as an additive rather than relying on the insoluble Te$^{IV}$O$_2$ to dissolve as was the case initially. A prediction was made that the use of Te$_2^{IV}$O$_4$.HN0$_3$ would prevent formation of the flaky material observed as a result ofTe$^{IV}$O$_2$ addition. Tellurium (IV) nitrate was not used in the original trial (Section 4.2.1) because it was unavailable from regular chemical suppliers therefore, it required synthesis before it could be used. The production and isolation of tellurium nitrate involved the vigorous mixing of tellurium metal powder in concentrated nitric acid, producing a white precipitate, Te$_2^{IV}$O$_4$.HN0$_3$. PXRD of the product was able to identify the material as being tellurium nitrate with an orthorhombic, Pnma, unit cell and dimensions a = 14.55, b = 8.77, c = 4.45 Å.

Once synthesised the tellurium nitrate was used as an additive to ZM synthesis over a range of concentrations (Figure 4.6). PXRD identified the product in each case as ZM with no other crystalline species present and SEM confirmed the absence of any tabular by-product material. The crystalline product was well formed ZM crystals which
SAED confirmed were elongated along the [001] axis (Figure 4.7). Increasing the concentration of tellurium(IV) nitrate caused the aspect ratio of the ZM crystals to rise from 1.1 at 0 mol % additive to 4.3 at 15 mol % additive. However, the elongation only slightly increased further at higher additive concentrations (Table 4-4). Comparison of the effect of Te^IV_2O_2 and Te_2^IVO_4·HNO_3 revealed that at the same additive concentration Te_2^IVO_4·HNO_3 caused much greater ZM elongation. The absence of the flaky material when Te_2^IVO_4·HNO_3 additive was used and the presence of the flaky material as a result of the use of Te^IV_2O_2 suggested that insoluble Te^IV_2O_2 was the cause. The wheat-sheaf morphology was again not observed for the elongated product ZM crystals.
Figure 4.6 SEM micrographs of the influence of tellurium nitrate on ZM synthesis. A = 5 mol %  B = 15 mol %  C = 30 mol %
Figure 4.7 (Left) TEM image of a shard of ZM synthesised in the presence of tellurium nitrate additive with the direction of elongation shown. (Right) SAED pattern from which the [001] axis direction was confirmed as being parallel to the axis of elongation.

<table>
<thead>
<tr>
<th>Additive Concentration</th>
<th>Average Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mol %</td>
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</tr>
<tr>
<td>5 mol %</td>
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<td>15 mol %</td>
<td>4.3</td>
</tr>
<tr>
<td>30 mol %</td>
<td>4.5</td>
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Table 4-4 Table showing the aspect ratio of ZM crystals produced in differing concentrations of $\text{Te}_2\text{O}_4\text{HNO}_3$ additive
The ZM crystals produced in the presence of different concentrations of tellurium(IV) nitrate were analysed using PXRD. The absence of CPM and flaky solids in the sample made this analysis possible. The resultant diffraction patterns demonstrated how the elongation of crystals in a sample can change the intensity of PXRD reflections (Figure 4.9). Preferential orientation of the elongated crystals during the sample preparation was responsible for the change in diffraction peak intensities (Figure 4.8). PXRD sample preparation generally causes elongated crystals to lie flat along their long axis in the sample holder. For ZM this causes the X-ray beam to preferentially sample crystal lattice planes parallel to the elongated [001] axis and can be used as an indication of crystal elongation (Figure 4.9). Lattice planes perpendicular to the [001] axis are less likely to be exposed to the sampling X-ray beam because the preferential orientation of elongated crystals means that they are at right-angles to the angle of incidence.

Figure 4.8 (Left) Photograph of a PXRD sample holder with a prepared sample of ZM in the centre. (Right) SEM micrograph of elongated crystals which had been prepared in the same way. Micrograph shows the preferential orientation of elongated crystals when flattened during PXRD sample preparation.
Figure 4.9 Set of PXRD patterns over same range of angles (2Theta) and intensities. Figure shows the evolution of the heights of the different reflections as the crystals become increasingly elongated. Any reflection with [001] axis character is inhibited.
Figure 4.10 Schematic showing how the orientation of a crystal which is elongated along the [001] axis affects the probability of the X-ray beam reflecting off a specific lattice plane. Figure shows an elongated crystal lying along its long [001] axis (A / B) and how the (100) lattice planes are sampled (A) and the (001) lattice plane are not (B). C shows the improbable orientation of the crystal required for the (001) lattice planes to be sampled.
4.2.2.3 The Effect of Telluric(VI) Acid as an Additive on ZM Synthesis

Another tellurium containing small molecule, telluric acid (Te(VI)(OH)_6) was tested as an additive. It was thought that nitric acid, being a strongly oxidizing solution, might have converted tellurium(IV) dioxide to telluric(VI) acid in the initial experiments (Equation 4-1) and therefore, telluric acid might have been the active species in the elongation of ZM when Te(IV)O_2 was used as the additive.\(^5\)

\[
\text{TeO}_2 + 2\text{HNO}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{Te(OH)}_6 + 2\text{NO}_2 \quad \text{Equation 4-1}
\]

The effect of telluric(VI) acid as an additive was tested at a range of concentrations (Figure 4.11). At an initial concentration of 2 mol % the Te(VI)(OH)_6 additive caused the product ZM crystals to be slightly elongated (Figure 4.11C), an effect which increased between 2 and 4 mol % Te(VI)(OH)_6 (Figure 4.11C-E). At additive concentrations of 5 mol % and above the aspect ratio of the product continued to increase (Table 4-5) however, the cuboidal prismatic morphology of the crystals became increasingly irregular and the crystals began to diverge at the termini (Figure 4.11G-J). Revealing a change in the general ZM crystal morphology from an elongated cuboidal prism to one which resembled a wheat-sheaf, similar to those found in simulant HAL. This suggested that the morphology influencing component was Te\(^{6+}\). The elongated and divergent nature of the product ZM crystals continued to increase as the telluric acid additive concentration was further increased. At telluric acid additive concentrations higher than 9 mol % the elongation resulted in crystals which had become so elongated that they were brittle at the thin centre, causing them to break into wedge-shaped crystals in most cases (Figure 4.11J). There were also increasing amounts of reagent CPM remaining in the product, indicating that the ZM synthesis was becoming...
increasingly hindered at higher Te$^{VI}$(OH)$_6$ concentrations. An experiment containing 50 mol % Te$^{VI}$(OH)$_6$ additive produced only CPM reagent, with no ZM solids present, proving the ability of Te$^{6+}$ to hinder ZM synthesis at > 9 mol %.

<table>
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<th>Additive Concentration</th>
<th>Average Aspect Ratio</th>
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<tbody>
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</tr>
<tr>
<td>0.4 mol %</td>
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</tr>
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</tr>
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</tr>
<tr>
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<td>7.3</td>
</tr>
<tr>
<td>7 mol %</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 4-5 Table showing the aspect ratio of ZM crystals produced in different concentrations of telluric(VI) acid additive. Additive concentration does not go past 7 mol % because crystals began breaking due to the presence of a brittle centre.
Figure 4.11 (1) SEM micrographs of ZM crystals synthesised in the presence of different concentrations of telluric(VI) acid additive. A = 0.4 mol %  B = 1.0 mol %  C = 2.0 mol %  D = 3.0 mol %  E = 4.0 mol %  F = 5 mol %
Figure 4.11 (2) cont. SEM micrographs of ZM synthesised in the presence of different amounts of 
telluric(VI) acid additive. G = 6 mol % H = 7 mol % I = 8 mol % J = 9 mol %

Figure 4.12 (Left) TEM image of a shard of ZM synthesised in the presence of 7 mol % telluric(VI) 
acid additive, the direction of elongation is shown. (Right) SAED pattern from which the [001] axis 
direction was calculated, which corresponds with the direction of elongation.
4.2.2.3.1 Elemental Analysis of ZM Syntheses in the Presence of Telluric VI Acid Additive

The concentration of zirconium, molybdenum and tellurium in solution, was measured using inductively-coupled plasma optical emission spectroscopy (ICP-OES). The typical concentration profile for zirconium and molybdenum during ZM synthesis was discussed in section 3.2.1 and was used as a comparison against synthesis incorporating Te\(^{VI}\)(OH)\(_6\) additive (0.4, 1, 2, 5, and 10 mol %) (Figure 4.13).

![Figure 4.13 Concentration profile of molybdenum in solution during ZM synthesis in the presence of 0.4, 1, 2, 5 and 10 mol % Te(OH) additive and a control. The concentration of molybdenum in the presence of 0, 0.4, 1, and 2 mol % Te\(^{VI}\) are all very similar and are hard to distinguish.](image)

When the Te\(^{VI}\)(OH)\(_6\) additive concentration was less than or equal to 2 mol % the trend for the concentration of molybdenum in solution, [Mo], was very consistent and almost identical with that of the control ZM synthesis (Figure 4.13). At the higher additive concentrations (5 or 10 mol %, Te\(^{VI}\)(OH)\(_6\)) the results showed a period at around 2:30 hours in which [Mo] was higher than the control (5 mol % =1860 ppm, 10 mol % = 2200 ppm, and Control = 760 ppm). This showed that a higher concentration
of molybdenum existed in solution when telluric(VI) acid was present at 5 mol % or more.

Previously, it was concluded that [Mo] was the rate limiting factor during this stage of ZM synthesis (Section 3.2.1) therefore, it was expected that a higher [Mo] would cause the rate of ZM synthesis to increase proportionally. However, calculations showed a slight decrease in the rate of ZM production during this period when compared with the control (Figure 3.3). In the presence of 5 mol % $\text{Te}^{\text{VI}}(\text{OH})_6$ the rate of ZM production was on average 33 % slower than the control, indicating that $\text{Te}^{\text{VI}}(\text{OH})_6$ inhibited ZM production. Examination of the final reagent concentrations revealed the product yield was also lower than expected because the final concentration of $[\text{Zr}]$ was 220 ppm and 500 ppm for the samples containing 5 and 10 mol % $\text{Te}^{\text{VI}}(\text{OH})_6$ additive respectively whereas the control was 50 ppm upon completion of the reaction. Therefore, the presence of telluric(VI) acid reduced the final yield by 16.7 % at 10 mol % $\text{Te}^{\text{VI}}(\text{OH})_6$.

During the latter stages of ZM synthesis (> 35 hours) the [Mo] increased when in the presence of 5 and 10 mol % telluric acid additives (Figure 4.14). A slight increase in [Mo] was expected (Section 3.2.1) but the [Mo] roughly doubled from hour 35 to the end. During this period the concentration of tellurium in solution, [Te] also increased slightly. Whereas before 35 hours the trend for [Te] indicated that tellurium was being removed from solution and deposited into the solid phase. However, [Te] increased when ZM growth slowed, indicating that tellurium was released back into solution and revealing that tellurium removal from solution during ZM synthesis was reversible.

Elemental analyses of the bulk ZM crystals produced in the presence of different amounts of telluric(VI) acid additive were achieved by dissolving the samples in strong
alkaline solution over two days. ICP-OES analysis of the product solution revealed a large concentration of tellurium in the bulk solid. X-ray photoelectron spectroscopy (XPS) was also used to analyse the concentration of tellurium on the surface of the product crystals. Comparison of these results revealed a higher relative concentration of tellurium on the surface of the crystals than the crystal bulk. This result indicated that there was a noticeable amount of irreversible tellurium adsorption occurred on ZM crystal surfaces but the majority of tellurium attachment to ZM crystals was temporary.

In summary, elemental analysis of the Te$^{6+}$ additive experiments revealed that a higher than normal [Mo] did not cause increased ZM growth as expected and that the presence of Te$^{6+}$ prevented the reaction from going to completion. This was a strong indication was that there was a soluble species forming in solution which made molybdenum reagents unavailable for ZM synthesis but which allowed tellurium to reversibly bind to the growing ZM crystal surfaces.

![Graph showing concentration profile of ZM synthesis](image)

**Figure 4.14** Concentration profile of ZM synthesis in the presence of 10 mol % Te(OH)$_6$ additive
4.3 DISCUSSIONS

The results described in the previous section revealed the extent by which tellurium additives were able to affect the morphology of ZM crystals, showing a strong preference for causing an elongation of the crystals along the [001] axis. Of the different tellurium species tested telluric(VI) acid exhibited the most influence on ZM. Telluric(VI) acid caused the formation of crystals with a range of morphologies and aspect ratios. There existed no previous research into how the tellurium might have affected the growth of ZM crystals therefore, the mechanism by which Te\textsuperscript{VI}(OH)\textsubscript{6} effected ZM synthesis was investigated and the conclusions discussed below.

4.3.1 IDENTIFICATION OF MOLYBDENUM AND TELLURIUM CONTAINING SPECIES

ICP-OES indicated the presence of a molybdenum and tellurium (Mo-Te) containing species during the synthesis of ZM when in the presence of \( \geq 5 \text{ mol \%} \) telluric(VI) acid additive. SEM imaging revealed that the Mo-Te species had an effect on the final morphology of ZM crystals and XPS revealed a high concentration of tellurium on the surface of the crystal. Connections had previously been established between Zr, Mo and Te during investigations into the formation of solids in simulant HAL however, the results provided only an indication of perceived influence upon the precipitation of HAL solids\textsuperscript{12}.

Research revealed that the Mo-Te species was probably a polyoxometalate (POM) cluster material, often referred to as hexamolybdatellurate [TeMo\textsubscript{6}O\textsubscript{24}]\textsuperscript{6} which is known to self-assemble quickly in acidic solutions containing telluric acid and an excess of molybdates\textsuperscript{13}. In most cases all free molybdates and tellurates in a solution were seen to form hexamolybdatellurate POM clusters in this way\textsuperscript{14}. Typically POM
clusters are formed when octahedral metalate ions aggregate via condensation reactions, sharing corners, edges and occasionally faces.

Hexamolybdatellurate is an Anderson-type POM cluster which are composed of six metalate octahedra arranged hexagonally around a central heteroatom octahedron in a planar fashion (Figure 4.15).\textsuperscript{15,16} The central heteroatom octahedron of hexamolybdatellurate is made up of a central Te\textsuperscript{6+} bound to six molybdate octahedra via Mo-O-Mo edge-shared bridging-oxygens. In the [TeMo\textsubscript{6}O\textsubscript{24}]\textsuperscript{6-} structure, there are two terminal molybdate octahedral oxygens, two-shared Mo-O-Mo bridging oxygens and two corner-shared oxygens that are shared between two molybdate octahedra and the central tellurate. POM units are also present in CPM, a reagent for ZM synthesis. The main body of CPM is a Keggin-type POM cage, 12 x molybdate octahedra around a central heteroatom (Figure 4.16).
Figure 4.15 Ball and stick (Left) and Polyhedral (Right) representation of hexamolybdotellurate, an Anderson POM cluster. Oxygen = Red. Metalate (Molybdenum) = Purple. Heteroatom (Tellurium) = Orange. Polyhedral representation is comprised of $\text{MO}_6$ octahedra (Green) arranged in a planar manner around central $\text{TeO}_6$ octahedra (Red).

Figure 4.16 Ball and stick (Left) and Polyhedral (Right) representation of a CPM Keggin POM cluster. Oxygen = Red. Metalate (Molybdenum) = Purple. Heteroatom (Phosphorous) = Orange. Polyhedral representation is comprised of $\text{MO}_6$ octahedra and shows a cage surrounding the central heteroatom.
Potentiometric methods have determined the relationships between [TeMo₆O₂₄]⁶⁻ and acidity (Equations 4-2a-c and 4-3). In strongly acidic environments hexamolybdotellurate becomes doubly protonated at the central tellurate octahedron. The results suggested that this state was maintained at pH values closer to those of ZM synthesis and lower than those used in the study. However, it was stated that the amount of [TeMo₆O₂₄]⁶⁻ in solution decreased as acidity was increased from 100% at pH=5 to around 75% at pH=2.5 and 50% at pH=0. Indicating that the doubly protonated hexamolybdotellurate TeMo₆O₂₄(H)₈ is less stable than the singly and unprotonated complexes. The conditions encountered during ZM synthesis (pH = -0.47) suggest that the amount of hexamolybdotellurate present would probably be less than 50 %, and where present it would exist in the doubly protonated form, [TeMo₆O₂₄(H)₈]²⁺.

\[
6\text{MoO}_4^{2-} + \text{Te}^{6+} + 6\text{H}^+ \rightleftharpoons \text{TeMo}_6\text{O}_{24}(\text{H})_6 \quad 7 < \text{pH} > 5 \quad \text{Equation 4-2a}
\]

\[
\text{TeMo}_6\text{O}_{24}(\text{H})_6 + \text{H}^+ \rightleftharpoons \text{TeMo}_6\text{O}_{24}(\text{H})_7^+ \quad 5 < \text{pH} > 2.5 \quad \text{Equation 4-2b}
\]

\[
\text{TeMo}_6\text{O}_{24}(\text{H})_7^+ + \text{H}^+ \rightleftharpoons \text{TeMo}_6\text{O}_{24}(\text{H})_8^{2+} \quad 2.5 < \text{pH} > ? \quad \text{Equation 4-2c}
\]

The final all-inclusive equation given as:

\[
p\text{H}^+ + q\text{MoO}_4^{2-} + r\text{Te(OH)}_6 \rightleftharpoons (\text{H}^+)p(\text{MoO}_4^{2-})q[\text{Te(OH)}_6]^r \quad \text{Equation 4-3}
\]
4.3.2 POLYOXOMETALATE COMPLEXATION

Investigation was made of the possible influences which hexamolybdotellurate might have on ZM synthesis and crystal growth through investigation of POM complexation. The extensive internal hydrogen-bonding of Anderson-type POM clusters plays an important role in the stabilization of the extended structure of hexamolybdotellurate. The oxygen atoms act as proton acceptors giving them the additional ability to form intermolecular hydrogen bonds allowing the \([\text{TeM}_6\text{O}_{24}]^{6-}\) anion to act as a multidentate ligand. Transition metals and lanthanides have been known to form complexes with hexamolybdotellurate. For lanthanide complexes in all cases the lanthanide metal centre binds to the terminal oxygens on hexamolybdotellurate generally producing a 1D chain or a 2D layered architecture. The only transition metal complexes able to form at bench conditions are linked by \(\text{Co}^{2+}\) ions and form a 1D polymer chain in which the \(\text{Co}^{2+}\) binds to 2 terminal oxygens from \([\text{TeM}_6\text{O}_{24}]^{6+}\) anions at equatorial sites. Gao was the first to attempt to use hydrothermal techniques to attach Anderson-type POMs and metal centres. The result was highly symmetrical structures made from the binding of hexamolybdotellurate to first row transition metals and \(\text{Ag}^+\) in a 3D structure.

Keggin-type polyoxomolybdates, similar to CPM, show ability comparable to hexamolybdotellurate to complex rare earth elements and transition metals. However, the history of keggin transition metal complexation and the instability of the hexamolybdotellurate complexes in highly acidic environments makes it probable that there is no attachment of hexamolybdotellurate ligands by zirconium during normal ZM synthesis or lanthanides during experiments containing simulant HAL.
The formation of a number of interesting complexes was predicted by research investigating the vibrational and Raman structures of hexamolybdotellurates using density functional theory. However, the conditions required for these complexes to form were not representative of ZM formation in HAL. The structures included infinite 1D chains of TeMo$_6$O$_{24}$-Te(OH)$_6$ formed in excess telluric acid, the strong H-bonds between Te$^{VI}$(OH)$_6$ hydroxyl groups and oxygens in the POM allowing this structure to form. The retardation of ZM synthesis observed in the presence of more than 10 mol % Te$^{VI}$(OH)$_6$ is thought to occur because the excess telluric acid allows the formation of telluric acid-linked hexamolybdotellurate chains (-TeMo$_6$O$_{24}$-Te(OH)$_6$-). These would make the hexamolybdotellurate molecules more stable and less prone to molybdate release. A number of other Mo-Te species are also known to form, including nanorods and films, but all in conditions which are not representative of ZM synthesis.

4.3.2.1 MOLYBDENUM COMPLEXATION

The indication from investigation of the complexation of transition metals was that hexamolybdotellurate would not bind with the zirconyl units. Therefore, the influence of hexamolybdotellurate on ZM synthesis must involve affecting either a molybdate species in solution or a crystal growth face.

The reversible adsorption of tellurium from ZM crystal surfaces expected from the results of ICP-OES and XPS analysis of ZM synthesis (Section 4.2.4) could not be explained by the comparison of the facial intramolecular atomic distances. Measurement of the distances between oxygen and molybdate centres on the surface of both hexamolybdotellurate and the prevalent faces of ZM revealed no obvious lattice matching.
At high acidities hexamolybdotellurate is known to be unstable breaking down to release $\text{H}_2\text{TeO}_4$ and $\text{Mo}_2\text{O}_5^{2+}$ units. The molybdate fragments produced by this breakdown closely resemble the $\text{Mo}_2\text{O}_5^{2+}$ units present in ZM and other molybdate structures and cannot be differentiated spectroscopically. This similarity in atomic arrangement suggests that $\text{TeMo}_6\text{O}_{24}^{6-}$ could reversibly absorb at $\text{Mo}_2\text{O}_5^{2+}$ attachment sites on ZM crystal growth faces. This would cause face specific attachment of hexamolybdotellurate to both (001) and (001) crystal faces because as in section 3.2.3 the (001) face is the most susceptible to $\text{Mo}_2\text{O}_5^{2+}$ binding (Figures 4.17 and 4.18). This preferential attachment of hexamolybdotellurate to the growth faces along the [001] axis and the instability of the hexamolybdotellurate molecule could mean that any molybdates present would attach to ZM growth surfaces in this way and then breakdown releasing the bound $\text{Mo}_2\text{O}_5^{2+}$. 
Figure 4.17 Proposed scheme for hexamolybdotellurate (TeMo$_6$O$_{24}$) binding to (001) face of ZM crystal during growth of ZM crystals in the presence of hexamolybdotellurate. Red pentagonal bipyramids = ZrO$_2$, Green octahedra = MoO$_6$, and Blue octahedra = TeO$_6$. The approach of hexamolybdotellurate is shown in A. B shows how the molybdates on the tellurate can bind to the zirconyl unit. C shows how thermal breakdown of the tellurate could leave the molybdate still attached to the ZM growth face, a rotation of the molybdate octahedra on release from hexamolybdotellurate aligns the Mo$_2$O$_6^{2-}$ unit properly inside the ZM unit cell.
Figure 4.18 Diagram showing the proposed binding of hexamolybdotellurate to ZM along either the [100] or [010] axis of the crystal. Figure displays how the bulk of the tellurate would hinder its attachment at the (100) or (010) crystal faces.
4.4 CONCLUSIONS

Of the inorganic HAL components tested, only tellurium influenced the growth of ZM and in some cases tellurium produced some very pronounced effects on ZM morphology. Tellurium$^{IV}$ dioxide addition resulted in a slight elongation of ZM along the [001] axis but also produced a flaky material as a by-product at higher concentrations. The use of Te$^{IV}$O$_2$ was refined by the synthesis of tellurium$^{IV}$ nitrate, which proved a better morphology-affecting agent than tellurium$^{IV}$ dioxide producing moderately elongated ZM without the presence of any by-products. When trialled telluric$^{V}$ acid caused ZM crystals to become elongated along the [001] axis even at low concentrations and resulted in the morphology changing from cuboidal prisms to elongated wheat-sheaves. This morphological change was such that it is thought to be able to cause improved sedimentation rates and formation of an open packed settled bed of solids in solution. The tellurium concentration in HAL is roughly 20 mol % with respect to the possible maximum zirconium molybdate yield. From the result contained in this section it can be assumed that there is a high possibility that any or some of the tellurium present in HAL will have an effect on ZM crystallization. However, these results cannot be directly applied to HAL systems because many of the other constituent species will likely form complexes with TeMo$_6$O$_{24}$. Detailed speculation of the outcome of chemical reactions of Zr, Mo, and Te in a mixture which is as complex, restricted, and dangerous as HAL are difficult to conclude and only direct sampling of actual ZM samples from HAL and in depth investigations using simulant systems will provide those answers.
4.5 References


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Chapter 5

The Influence of Organic Additives on Zirconium

Molybdate Crystal Growth
5 THE INFLUENCE OF ORGANIC ADDITIVES ON ZIRCONIUM MOLYBDATE CRYSTAL GROWTH

5.1 INTRODUCTION

The use of organic molecules to direct and influence crystal growth is a well-studied field of research. Additive molecules chosen to influence crystallization and the growth of organic crystals are typically identified by rational adjustment of crystal growth unit stereochemistry used to customized the molecule for attachment to specific growth faces. The outcome is typically enhanced or hindered growth at certain crystal faces enabling an amount of control over crystal growth habits and subsequently the final morphology of the crystal. For example, the use of additives which mimic and then block crystal growth sites are typically employed for controlled growth inhibition or retardation of a specific face. There is however, no general theory to predict the influence of a particular additive or at what concentration the additive would become effective. Modification of the stereochemistry of inorganic crystal growth units is relatively less effective than for organic units because inorganic units generally possess little scope for stereochemical manipulation.

For ZM synthesis any influence from organic additives would be expected to occur in solution with inorganic-organic complex formation. These complexes would then be expected to affect the crystallization by providing supplementary stereochemical characteristics to the existing inorganic reagent molecules. However, the formation of inorganic-organic complexes would also be expected to stabilize the reaction intermediates, which would in turn be expected to alter the solubility of the affected species and their supersaturation values. Therefore, the use of organic additives could
influence crystal morphology as a result of changing the crystal growth mechanism via altering the nucleation points and growth rates.\(^8\)

During this study of ZM the organic additives chosen for use as potential crystal growth influencing agents were in the majority of cases restricted to those known to specifically interact with molybdates and zirconyls. The intention was that the additive would interact with the ZM reaction intermediates as specifically as possible, preventing any avoidable interaction with the other solids known to form in HAL. However, HAL contains a number of zirconate solids including zirconium nitrate and zirconium phosphate, something which excludes the use of a zirconyl-specific additive because it could have an undesirable influence on the formation of other HAL solids. However, the only molybdate solids known to form in HAL are caesium phosphomolybdate (CPM) and zirconium molybdate (ZM) which are both present during a typical ZM synthesis reaction, allowing the effect of the molybdate-specific additive on all HAL solids to be wholly assessed simultaneously. However, a drawback of using many of the molecules which are known to interact with molybdate is that they are often good binding agents for other metal ions. Therefore, any subsequent testing of the effect of any additives on HAL would have to take place to allow any impact of the complexation to be assessed.

Currently the presence of any organic molecules in highly active waste streams, including HAL, is strictly controlled and generally kept as low as possible. This is because under radioactive bombardment, organic molecules can breakdown into a number of molecules including water, oxygen, carbon monoxide, dioxide, or similar units.\(^9,10\) The creation of \(\text{O}_2\) and \(\text{CO}_2/\text{CO}\) is itself not a problem but because they are gases at the conditions in question they can cause the formation of foam on the surface of the HAL. If uncontrolled the production of foam has the potential to carry highly
radioactive material through pressure releases and into unshielded parts of HALES plant, resulting in significant personal and environmental safety issues. It was for this reason that the use of organic additives as ZM synthesis habit modifying additives was initially excluded. However, an opportunity for the potential use of organic agents has since been identified which would reduce the risk of radiation release.

When a site which has regular contact with radioactive material, including HALES, comes to the end of its working life, all radioactive and harmful materials need to be removed from the infrastructure before it can be dismantled. This process is designed to leave a site "cold" and is called post-operative clean-out (POCO). The POCO of HALES is currently undergoing preliminary testing but it is already assumed that it would involve the removal via dissolution of any solids remaining inside vessels and pipework, including ZM. It has been decided that once the solids have been dissolved the solute would be transferred to a new location to allow the solids to be reprecipitated in a controlled environment. Reprecipitation will involve the re-acidification of what is expected to be highly alkaline solute and must take place to make the waste stream suitable for future vitrification and storage. The process of re-acidification is expected to cause significant foaming and it is at this point that the opportunity for the introduction of organic additives has been considered. The re-acidification vessels will be designed to contain any foam produced and therefore, any foam produced by the use of organic additives would not cause any problems. The work contained in this chapter reveals how selected organic additives effect ZM crystal growth and final product morphology.

A number of small organic molecules are capable of molybdate complexation in acidic environments including oxalic acid, malic acid and citric acid. These molecules all bind to molybdenyl ions using α-hydroxyl and α-carboxyl groups with the
involvement of β-carboxylic acid groups changing in each instance. Along with these molecules, other additives were chosen and trialled because they either possessed attributes which were similar to the molecules mentioned above or were commonly used multidentate ligands.

Citric acid, $C_6H_8O_7$ was chosen as an additive because its addition to an acidic solution of molybdenyl ions is known to produce a bicitrate-bound oxomolybdate molecule, citromolybdate (Figure 5.1).$^{12,15}$ Other molybdenum : citric acid complexes have also been reported,$^{16-18}$ but none formed at the highly acidic conditions encountered during ZM synthesis. In citromolybdate, the cis-bound tridentate citric acid ligands bind to a molybdate centre situated on each side of the central Mo-O-Mo oxygen bridge. The product is a symmetrical complex where the citric acid ligands coordinate to each molybdenyl centre using the α-hydroxyl and α-carboxyl groups and half of the β-carboxylic acid group. The other half of the β-carboxyl participates in hydrogen bonding.

![Figure 5.1 Structure of citromolybdate](image)

Malic acid, $C_4H_6O_5$, possesses a structure similar to citric acid but with one less carboxylate group, it is also part of the citric acid cycle (Figure 5.2).$^{19}$ The loss of the carboxylate makes malic acid complexes less stable at lower pH ranges than their citric acid analogues. This is because malic acid cannot be further protonated limiting the
possible molybdenum : malic acid structural forms. For example, the formation constants for complexes with a molybdenum : malic acid ratio of [1:1] are roughly an order of magnitude smaller than the corresponding citratomolybdate (Figure 5.3).

Figure 5.2 Structure of malic acid

Figure 5.3 Structure of the various malatomolybdates which are reported to form over a range of concentrations and pH. The ratio of molybdenum : malic acid is shown beneath each structure.
Acetylsalicylic acid, $C_9H_8O_4$, has not been reported as specifically forming complexes with molybdates however, as a ligand it is similar to citric acid (Figure 5.4), because it possesses similar functional groups separated by comparable distances.

![Figure 5.4 Structure of acetylsalicylic acid](image)

Tartaric acid has long been known to complex molybdates in solution. In one example generating left and right handed double-helix structures of tartaromolybdates in the presence of lanthanide cations.\textsuperscript{13,21,22} Mononuclear tartaromolybdates form in solutions with pH values between 4.5 and 7. At lower pH levels dinuclear structures form in which the metal centres are separated from each other.\textsuperscript{23} These are quite different from the Mo-O-Mo oxygen bridged oxomolybdate, $[\text{Mo}_2\text{O}_3]^{2+}$, the intermediate molybdate of ZM synthesis and for citrato- / malatomolybdates in which molybdate centres are typically edge or corner sharing.

Oxalic acid was reported to form numerous complexes with molybdate octahedra including molybdenum : oxalic acid species with ratios 1 : 1, 1 : 2, 2 : 1, and 2 : 2 depending on the pH. Although the concentration and pH range of interest is not covered in literature the suggestion was that a 2 : 2 species, similar to the malatomolybdate 2 : 2 complex would form however, it is unlikely to form at the pH required.\textsuperscript{14,24}
Other additives trialled include, formic acid because it is reported to abstract Mo$_2$ units from the mixed-oxide molybdenum blue species including (PMo$_4^{5+}$Mo$_8^{6+}$O$_{40})^7$-, by substitution with two H$_2$O groups.\textsuperscript{25} EDTA because it has a good history of forming tri-metallic complexes. Succinic acid is reported to form complexes with single Mo$^{6+}$ ions.\textsuperscript{13} Sorbitol is a surfactant molecule with hydroxyl groups spaced along a six-carbon backbone at distances similar to those of citric acid and malic acid. Sorbitol is also known to complex Mo$^{VI}$ and has been used previously to template the growth of MoO$_3$ crystals.\textsuperscript{26}
5.2 RESULTS AND DISCUSSION

5.2.1 ORGANIC ADDITIVES

Each of the organic molecules chosen for use as additives were individually introduced to discrete ZM syntheses using the method set out in section 2.3.4 which involved adding the required amount of additive at the start of a typical synthesis of ZM. An additive concentration of 10 mol % was chosen as a balance between the concentration being high enough so that any effect would be obvious and low enough to minimize the risk of foaming if the methods were applied industrially. The results of the addition of different organic additives to ZM syntheses are summarised in Table 5-1 and SEM micrographs of the products are presented in figure 5.5. The crystalline solids produced were identified in each case using PXRD and the relative amounts of ZM and CPM judged qualitatively in this manner. There were a number of distinctive outcomes from the addition of the different additives which have been grouped and classified as:

A- No effect, product was mainly ZM with normal morphology

B- Some effect on ZM morphology, product was mainly CPM reagent

C- Large effect on ZM, product was exclusively ZM with altered morphology
Figure 5.5 SEM micrographs of the product of initial trials of each different organic additive to ZM synthesis. A = Formic acid, B = Oxalic acid, C = Malonic acid, D = Maleic acid, E = Succinic acid, F = Malic acid, G = Tartaric acid, H = Acetylsalicylic acid, I = Sorbitol, J = Citric acid, K = EDTA. The other material present on the surfaces of some of the ZM crystals was CPM.
<table>
<thead>
<tr>
<th>Additive Molecule</th>
<th>IUPAC Name</th>
<th>Molecular Formula</th>
<th>Formula Weight (g/mol)</th>
<th>Comments on Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanoic Acid</td>
<td>Formic Acid</td>
<td>CH$_2$O$_2$</td>
<td>46.03</td>
<td>A</td>
</tr>
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<td>Ethanedioic Acid</td>
<td>Oxalic Acid</td>
<td>C$_2$H$_2$O$_4$</td>
<td>90.03</td>
<td>A</td>
</tr>
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<td>Malonic Acid</td>
<td>Propanedioic acid</td>
<td>C$_3$H$_4$O$_4$</td>
<td>104.06</td>
<td>A</td>
</tr>
<tr>
<td>Maleic Acid</td>
<td>(Z)-Butenedioic acid</td>
<td>C$_4$H$_4$O$_4$</td>
<td>116.07</td>
<td>A</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>Butanedioic acid</td>
<td>C$_4$H$_6$O$_4$</td>
<td>118.09</td>
<td>A</td>
</tr>
<tr>
<td>Malic Acid</td>
<td>Hydroxybutanedioic acid</td>
<td>C$_4$H$_6$O$_5$</td>
<td>134.09</td>
<td>B</td>
</tr>
<tr>
<td>Tartaric Acid</td>
<td>2,3-Dihydroxybutanedioic acid</td>
<td>C$_4$H$_6$O$_6$</td>
<td>150.09</td>
<td>B</td>
</tr>
<tr>
<td>Aspirin</td>
<td>Acetylsalicylic acid</td>
<td>C$_9$H$_8$O$_4$</td>
<td>180.16</td>
<td>B</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>(2S,3R,4R,5R)-Hexane-1,2,3,4,5,6-hexol</td>
<td>C$<em>6$H$</em>{14}$O$_6$</td>
<td>182.17</td>
<td>B</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>3-Carboxy-3-hydroxypentanedioic acid</td>
<td>C$_8$H$_8$O$_7$</td>
<td>192.12</td>
<td>C</td>
</tr>
<tr>
<td>EDTA</td>
<td>2,2',2''-(Ethane-1,2-diyldinitrilo)tetraacetic acid</td>
<td>C$<em>{10}$H$</em>{16}$N$_2$O$_8$</td>
<td>292.24</td>
<td>A</td>
</tr>
</tbody>
</table>

Table 5-1 Summary of the organic molecules trialled as additives to ZM synthesis for habit modification of ZM crystals and the general results of each.
The results show that in most cases the organic additives had no apparent effect on ZM synthesis, leaving a product which strongly resembled the cuboidal control ZM product featured in section 3.2.1 (Figure 5.5A-E). Some of the additives appeared to hinder the synthesis of ZM leaving mainly the reagent CPM as product after adequate time had been allowed for the reaction to go to completion. This was the case for tartaric acid and sorbitol (Figure 5.5G+I), which appeared to slow or hinder the production of ZM. The final product of which contained mainly CPM reagent with only small amounts of unaltered cuboidal ZM. Malic acid also appeared to slow the formation of ZM but in this case the product contained much greater amounts of ZM alongside the CPM reagent (Figure 5.5F). The addition of malic acid also produced ZM crystals with an elongated morphology. However, the most remarkable alteration of ZM morphology came from the addition of citric acid which, whilst causing a notable degree of elongation to the ZM product, also appeared to not retard ZM synthesis. The use of citric acid was further examined in section 5.2.2.

Consideration of HALEs challenges and limitations meant that impedance of the synthesis of ZM was not considered a desirable effect of additive introduction. This is because there is a lot of caesium in HAL and half of that caesium is the radioactive isotope $^{137}\text{Cs}$ which is initially present as caesium phosphomolybdate, CPM before the formation of ZM. The synthesis of ZM is initiated when CPM is broken down in post-evaporator HAL, a process which releases the caesium counter cations from CPM into solution (Chapter 3.2.2) therein solubilising of the highly radioactive caesium. Solubilisation disperses the $^{137}\text{Cs}$ isotopes homogeneously in the vessel, preventing the build-up of heat producing elements in settled HAL solids, something which causes a high corrosion rate. Therefore, anything which might hinder the synthesis of ZM and subsequently prevent $^{137}\text{Cs}$ solubilisation would not aid HAL solids management.
5.2.2 CITRIC ACID

The influence of citric acid on ZM synthesis was notable because it was the only additive from the trial which produced ZM with significantly altered morphology and without apparent hindrance of ZM synthesis, this result was unique amongst the additives tested.

The products of ZM synthesis in the presence of citric acid additives (10, 20, and 40 mol %) can be seen in figure 5.6. The identity of the crystalline samples present was confirmed using PXRD. SEM imaging of the product revealed ZM crystals which were elongated and possessed a central grain boundary. At 10 mol % citric acid the crystals were well-formed, moderately uniform in size with an obvious central grain boundary, and an average aspect ratio of 4.7 (Figure 5.6A). At 20 mol % citric acid the ZM crystals were thinner than the 10 mol % sample with an aspect ratio of 7.6. The morphology of the crystals at 20 mol % were less regular than at 10 mol % but the crystals still possessed a central grain boundary in most cases (Figure 5.6B). At 40 mol % citric acid the ZM crystals produced were smaller than the others but they also exhibited a large aspect ratio of 8.9, the presence of a grain boundary could not be confirmed in all cases (Figure 5.6C).

PXRD was used to qualitatively assessed the amounts of CPM and ZM and in the products of the 10 / 20 mol % additive samples where there were trace amounts of CPM reagent remaining, similar to the amount of CPM in a control sample. However, the ratio of CPM to ZM in the product was considerably higher at 40 mol % citric acid additive. At 20 mol% citric acid some product crystals resembled the wheat-sheaves produced during the use of telluric acid additives (Section 4.3.3)
Figure 5.6B insert), but the majority of crystals maintained the elongated square-based prism morphology at high citric acid concentrations. The elongation axis of the crystals was identified as the
Figure 5.6 SEM micrographs of the products of different concentrations of citric acid additive in ZM synthesis. A = 10 mol %, B = 20 mol % (Insert is close-up of a crystal), C = 40 mol %.

<table>
<thead>
<tr>
<th>Additive Concentration (mol %)</th>
<th>Average Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.7</td>
</tr>
<tr>
<td>20</td>
<td>7.6</td>
</tr>
<tr>
<td>40</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 5-2 Summery of the effect of different concentrations of citric acid additive on the average aspect ratios of ZM crystals

Figure 5.7 (Left) TEM image of a shard of a ZM crystal which had been grown in the presence of citric acid (10 mol %). Arrows indicate direction of elongation and the directions of the crystal axis. (Right) SAED pattern taken of the image, with the diffraction peaks identified. The [001] axis direction was confirmed using SAED as being perpendicular with the axis of elongation.
5.2.2.1 ELEMENTAL ANALYSIS

Inductively-coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the concentration of zirconium and molybdenum in solution during ZM synthesis in the presence of citric acid (10 mol %) (Figure 5.8). The results revealed that there was a peak in the concentration of molybdenum in solution, [Mo], early in the reaction. An initially high [Mo] was expected because nucleation does not occur until [Mo] reaches 600 ppm. However, the [Mo] peak during ZM synthesis in the presence of 10 mol % citric acid was roughly 2.5 times that of the control during the same period, reaching 1800 ppm compared to 720 ppm for the control. The peak in molybdenum concentration also occurred earlier in the presence of citric acid than in the control, indicating that more molybdates were present in solution, although possibly stabilized as citratomolybdate. In a citric acid-free system once ZM nucleation had started the [Mo] level dropped to a stable base level. This low concentration was equivalent to that of the control because any free molybdates would quickly be attached to ZM, meaning that the molybdate concentration was limited by the dissociation rate of CPM. In the citric acid containing synthesis the decrease of the [Mo] to a base level similar to that of the control meant that the citratomolybdate molecules were not acting to stabilize molybdates in solution and had possibly become denatured or been taken into the ZM crystals.
Figure 5.8 Graph showing separately the progression of the concentration of molybdenum and zirconium in solution during the synthesis of ZM in an additive-free control system and in the presence of citric acid (10 mol %).

During the ICP-OES investigation of the control ZM synthesis, [Mo] was assigned as the rate-limiting factor (Section 3.2.1.1). In the presence of citric acid the [Mo] was 2.5 times the control and therefore, the rate of ZM production was expected to increase accordingly. Using the method stated in section 3.2.1.2 the trend for reactant uptake and ZM production in the presence of citric acid (10 mol %) was then plotted against the control (Figure 5.9). Comparison shows that during the early stages of ZM synthesis in the presence of citric acid (10 mol %), there was an increase in the rate of ZM synthesis of 33.5 % over that of the control for the same period (0 - 10 hours). However, comparison of the overall rates for the first 24 hours revealed that citric acid (10 mol %) caused a decrease of 8.4 % relative to the control and the 33.5 % rate increase over the initial 10 hours can be considered modest when compared to the 2.5
times increase in [Mo]. The persistently high [Mo] during the initial 10 hours of ZM synthesis and the slow response of [Zr] to this surplus was considered an effect of the stabilization of the molybdates attributed to citratomolybdate complex formation. The overall 4.8 % yield decrease after completion of the reaction can be attributed to the remaining molybdates being bound as citratomolybdates, stabilizing them in solution. However, the modest initial rate increase did not explain the formation of elongated crystals and the persistence of the central grain boundary in the final crystals.

Figure 5.9 Graph showing the difference in the reaction progress of the citric acid (10 mol %) influenced and control ZM syntheses. Calculated from the amount of zirconium present at any point which is used to indicate the amount of ZM synthesised.
5.2.2.2 MECHANISM OF CITRIC ACID CONTROL OF ZM GROWTH

Citric acid was chosen as an additive for ZM synthesis because it was thought that it might form a citratomolybdate complex with oxomolybdate (Mo$_2$O$_5^{2+}$) in acidic solution.$^{12,15}$ ICP-OES analysis has shown that molybdenum was initially present at high concentrations in citric acid-containing solutions but that the rate of ZM formation was less than could be expected. However, this did not wholly explain the morphology observed in the ZM product. A mechanism describing the potential attachment of a citratomolybdate complex to a crystal surface of ZM was devised in attempt to provide a possible explanation of the crystal growth habit observed (Figure 5.10).

Figure 5.10 shows how CPM could initially breakdown releasing caesium, phosphoric acid, and oxomolybdate into solution (Figure 5.10A). It also expresses how if Mo$_2$O$_5^{2+}$ was present it could preferentially bind to some of the ZM crystal growth faces, something previously covered in chapter 3 (Figure 5.10B). The introduction of citric acid to the synthesis as an additive, (Figure 5.10C) might have been able to bind the oxomolybdate intermediate [Mo$_2$O$_5$]$^{2+}$ into a citratomolybdate complex (Figure 5.10D).$^{15}$ Oxomolybdate, [Mo$_2$O$_5$]$^{2+}$, is non-centrosymmetric due to the bent central Mo-O-Mo bond, which has an angle of 144.7° in solution (Figure 5.12).$^{24,27}$ If some of the [Mo$_2$O$_5$]$^{2+}$ was complexed by citric acid ligands to form citratomolybdate complex then there is precedent in previous studies that the bent central bond would be retained at an angle which would be more representative of the angle of the oxomolybdate unit once bound to ZM, 137.4°, making potential attachment more likely.$^{28}$
Figure 5.10: Overview of the proposed mechanism of citric acid influence on ZM synthesis.

Caesium phosphomolybdate

A

Nitric acid (3 Molar)
High Temperature (>60°C)

\[
\text{HO-PO-P-OH}
\]

6 \[\begin{array}{c}
\text{O}_2\text{MoO}_4^{2-} \\
\text{Zirconium}
\end{array}\] + Zirconium

\[
[100] \\
[010]
\]

OR
Citric Acid

B

\[\begin{array}{c}
\text{HOOC-CH(OH)COOH} \\
\text{HOOC-CH(OH)COOH}
\end{array}\]

C

\[\begin{array}{c}
\text{O}_2\text{MoO}_4^{2-} \\
\text{Zirconium}
\end{array}\] + Zirconium

\[
[001]
\]

D

equivalent to

\[\begin{array}{c}
\text{O}_2\text{MoO}_4^{2-} \\
\text{Zirconium}
\end{array}\] + Zirconium

\[
[001]
\]
Figure 5.11 Proposed mechanism for citric acid influence on the inhibition of molybdate attachment to the (100)/(010) crystal faces. The bound citric acid ligands block the terminal position of each molybdate centre preventing binding.

Figure 5.12 Diagram of the various Mo-O-Mo angles during the proposed mechanism of oxomolybdate addition to ZM via citratomolybdate formation.
The schematic shows how the angle of the bent central Mo-O-Mo bond and the steric hindrance of the citric acid groups only allow citratomolybdate bound molybdates to bind to the (001) crystal face of ZM (Figure 5.10E and 5.11). The bent central Mo-O-Mo bond inhibits citratomolybdate binding at the (001) face because the cis arrangement of the two citric acid ligands on citratomolybdate prevents any binding to the molecule on the convex side of the central Mo-O-Mo bond. Therefore, the result was that the only side of the oxomolybdate available for interaction was the concave side with respect to the central Mo-O-Mo bond. Consideration of the prominent ZM crystal faces revealed that the concave side of the oxomolybdate unit was only capable of binding to one face, the (001) crystal face (Figure 5.10E). After citratomolybdate groups become bound to the (001) face of ZM the steric hindrance of the citric acid groups prevents any subsequent growth on that face (Figure 5.10E). At the same time growth will continue as normal on the unhindered faces and stabilization of a particular face in this way can cause the formation of a grain boundary. The presence of the central grain boundary indicates the twinning of two crystals in most cases. Crystal twins are composed of two separate crystals which share some lattice points in a symmetrical manner. However, it is not certain that this is the case for these crystals because the use of additives does not always produce epitaxially-matched crystal pairs.

Typically, the twinning of crystals as a result of additive molecules occurs by stabilization of one or more crystal faces and is often controlled by the charge of the crystal surface. In these cases the charge on either terminus would be expected to be the same if the crystals are twins. This is because the whole crystal will be symmetrical.
about the central grain boundary and therefore, the terminal faces and their charges would be the same. This is only the case when the additive can bind to more than one crystal face. In the case of citric acid, the binding of the additive was thought to be face specific (Figure 5.10) therefore, the touching faces of the crystals are likely to be the (00\bar{1}) crystal faces and therefore, the crystals would be twins.
5.2.3 ALTERNATIVE ORGANIC ADDITIVES

The findings from the investigation into the effect of citric acid were used to help explain how the other organic additives which were tested (Figure 5.5, Table 5-1) affected ZM crystal growth and morphology.

5.2.3.1 MALIC ACID

When malic acid (10 mol %) was used as an additive to ZM synthesis, the product contained both ZM and CPM (Figure 5.14A) in which the relative concentration of CPM was more than would be expected (Figure 5.13). The ZM crystals in the product were elongated to a similar degree as the citric acid influenced samples (Table 5-3) but there was no evidence of a regular grain boundary. At 10 mol % malic acid the ZM product had an aspect ratio of over four. At 40 mol % malic acid the ZM product still maintained its regular elongated cuboidal form and the aspect ratio had increased to seven. However, CPM was a major product in these samples making accurate sampling of the crystal dimensions difficult, an effect which became more evident at higher concentrations. At 200 mol % malic acid additive concentration the product was mostly CPM reagent, with a few small ZM crystals present (Figure 5.14).
Figure 5.13 PXRD pattern of the product of ZM synthesis in the presence of 10 mol % malic acid. * indicates main reflection of CPM

<table>
<thead>
<tr>
<th>Additive Concentration (mol %)</th>
<th>Malic Acid Aspect Ratio</th>
<th>Citric Acid Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.2</td>
<td>4.7</td>
</tr>
<tr>
<td>40</td>
<td>7.1</td>
<td>8.9</td>
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</table>

Table 5-3 Summery of the effect of different concentrations of malic acid and citric acid additive on the average aspect ratios of ZM crystals
Figure 5.14 SEM micrographs of the products of different concentrations of malic acid additive to separate ZM syntheses. A = 10 mol %, B = 40 mol %, C = 200 mol %.
Explanations of the effect of malic acid on the products of ZM synthesis come from published literature on formation of malatomolybdates in acidic solution at equimolar and malic acid-rich ratios. Work on this topic does not however, cover acidities greater than pH 1, making prediction of the potential species present uncertain because ZM synthesis takes place at an acidity consistently around pH -0.48. The malatomolybdates which form in acidic systems include mononuclear MoO₃(mal)³⁻, MoO₂(mal)⁴⁻, dinuclear Mo₂O₆(mal)₂⁴⁺, Mo₂O₆(mal)(H₂O)₃⁻, and tetranuclear Mo₄O₁₁(mal)⁴⁻, Mo₄O₁₀(OH)(Hmal)⁴⁻ and their respective protonated forms some of which are shown in figure 5.3.

In a malic acid-rich system the indication was that a tetranuclear malatomolybdate complex with a molybdenum : malic acid ratio of 4 : 4 were the most prevalent complex at pH < 1. However, the study also indicates that a mononuclear malatomolybdate was also likely to be present but at much lower concentrations. Therefore, the binding of molybdates in a 4 : 4 tetranuclear malatomolybdate complex would likely cause their passivation a result of the steric hindrance of the attached malic acid groups. This hypothesis was supported by PXRD characterization of the product of 200 mol % malic acid identifying the product as mostly CPM reagent (Figure 5.14C).

At equimolar concentrations of molybdenum : malic acid the most prevalent malatomolybdate complex expected to be present in highly acidic solution is a tetranuclear 4 : 2 structure (Figure 5.3C). This tetranuclear complex is composed of two edge-sharing oxomolybdate couples bound by Mo-O-Mo and malic acid bridges. The molybdates in the 4 : 2 complex have some availability for reaction because the malic acid ligand would not provide as much hindrance as the 4 : 4 complex. The greater availability of molybdates in this complex increases the availability of the bound
molybdates to growing ZM crystals therefore, 4 : 2 complexes have a greater possibility of directly influencing ZM formation than 4 : 4.

The results of malic acid addition at high concentrations showed a retardation and almost total hindrance of ZM synthesis. The likely cause was the formation of 4 : 2 or 4 : 4 malatomolybdate complexes. The product of ZM synthesis under these conditions was ZM crystals with elongated morphologies, but unlike citric acid there was no central grain boundary present. This indicated that a different elongation mechanism was involved. One possible explanation came from the lower stability of malatomolybdates compared to citratomolybdates. Which meant that if malatomolybdates did bind to ZM crystal growth faces in a similar way to citratomolybdates the complex could breakdown. The result would be the release the malic acid ligands which would subsequently remove any hindrance of the attached crystals growth face, this would prevent the formation of a central grain boundary as seen with the more stable citratomolybdates.
5.2.3.2 ACETYSALICYLIC ACID

The results of acetylsalicylic acid addition to ZM syntheses at different concentrations (10, 40 and 200 mol %) can be seen in figure 5.16. At 10 mol % acetylsalicylic acid the ZM product appeared unchanged from the control except there was a higher than expected amount of CPM reagent present (Figure 5.15A) which was qualitatively estimated from PXRD (Figure 5.16). When the additive concentration was increased to 40 mol % there was a greater amount CPM reagent remaining in the final product but the ZM crystals had been moderately elongated and possessed an aspect ratio close to five (Figure 5.15B). An excess of acetylsalicylic acid additive (200 mol %) produced only CPM reagent in the final product (Figure 5.15C).

<table>
<thead>
<tr>
<th>Concentration of Additive (mol %)</th>
<th>Average Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.1</td>
</tr>
<tr>
<td>40</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 5-4 Summery of the effect of different concentrations of acetylsalicylic acid additive on the average aspect ratios of ZM crystals
Figure 5.15 SEM micrographs of the products of different concentrations acetylsalicylic acid addition to separate ZM syntheses. A = 10 mol %, B = 40 mol %. C = 200 mol %.
Figure 5.16 PXRD patterns showing the progress of amount of ZM and CPM in the product of ZM synthesis in the presence of different amounts of acetylsalicylic acid (10 mol %, 40 mol % and 200 mol %). (* indicate reflections produced by CPM, other reflections were attributed to ZM)
Elemental analysis of the concentration of zirconium and molybdenum in solution during the synthesis of ZM in the presence of acetylsalicylic acid revealed a 2.5 times increase in the initial [Mo] 1745 ppm (Figure 5.17). During this period the [Mo] was similar to that for 10 mol % citric acid additive (1750 ppm) but the high [Mo] did not last as long as that of citric acid, staying above control concentration for less than 2:30 hours compared to the 10 hours for citric acid (Figure 5.18). The build-up of molybdenum in the solution phase suggested that the acetylsalicylic acid was stabilizing the molybdates present. However, the rate of zirconium uptake from the solution phase into ZM suggested that the formation of ZM was unhindered and the initial [Mo] peak could be the result of nucleation delay (Figure 5.18). The overall rate of ZM production, calculated from the uptake of [Zr], suggested an increase of 648 % over the initial 2:30 hours, 80 % over the first 10 hours and 6.4 % over 24 hours. Therefore, the evidence was that acetylsalicylic acid was the cause of faster initial ZM synthesis although PXRD suggests that the reaction does not reach completion. Fast ZM synthesis has previously been seen to cause elongation of the product (Section 3.2.3), and was likely the cause in this case.
Figure 5.17 Graph showing separately the progression of the concentration of molybdenum and zirconium in solution during the synthesis of ZM in an additive-free control system and in the presence of acetylsalicylic acid (ASA) (10 mol %).

Figure 5.18 Graph showing separately the progression of the concentration of molybdenum and zirconium in solution during the synthesis of ZM in the presence of citric acid (10 mol %) and acetylsalicylic acid (ASA) (10 mol %).
5.2.3.3 Tartaric Acid and Sorbitol

The product of tartaric acid addition to ZM synthesis was predominately CPM, with only small amounts of ZM present (Figure 5.20A). The suggested potential tartaromolybdates\textsuperscript{13,21-23} do not appear applicable to the ZM synthetic mechanism suggested in chapter 3.2.3 and therefore, probably stabilized the CPM reagent and/or dissolved molybdates.

Sorbitol addition to ZM synthesis at low concentrations resulted in a product of mainly CPM reagent, revealing that the synthesis of ZM was highly hindered by sorbitol (Figure 5.19B). The reported strong binding of molybdates and the surfactant qualities of sorbitol suggest that any dissolved molybdates are strongly bound by sorbitol. The long carbon chain of the molecule which sterically hinders the approach of any other molecules, making it hard for any bound molybdate to react and form ZM.

Figure 5.19 SEM micrographs showing the product of ZM synthesis in the presence of A – Tartaric acid and B – Sorbitol (both 10 mol %). PXRD confirmed the product as CPM reagent in both cases.
5.3 CONCLUSIONS

The conclusion was that organic additives could affect a number of different effects on ZM synthesis whether it was reaction inhibition, ZM formation rate increase, or altering the morphology of ZM crystals. Specifically, citric acid and acetylsalicylic acid could potentially provide very advantageous results and aid HALES solid management. A number of hydroxycarboxylic acids additives were able to effect the synthesis of ZM, but the majority of other additives, including some classic crystallization affecting agents, did not cause any effects. Some of the additives trialled caused some alterations to the crystal morphology and provided reaction-inhibiting properties whereas others only inhibited ZM production. The only additive which at low concentrations did not inhibit ZM synthesis but affected a change in ZM crystal morphology was citric acid. In highly acidic solution the citric acid was able to complex the available molybdates and forms a stable product, citratomolybdate. The oxomolybdate centre of citratomolybdate has a structure which resembles the molybdate unit found in ZM structure, allowing it to be incorporated into the crystal at the (001) crystal face. The selectivity of the citric acid bound molybdates caused the formation of a central grain boundary in the crystals by blocking growth on the bound face, and resulted in the elongation of the ZM crystals. Of the other additives tested malic acid and acetylsalicylic acid both appeared to cause elongation of the ZM crystals. However, the product of malic acid addition contained high concentrations of the reagent CPM suggesting that the reaction had been hindered. At low concentrations, acetylsalicylic acid appeared to cause a catalytic-like effect on ZM synthesis, increasing the rate of ZM production and elongating the ZM crystal morphology. Higher concentrations of acetylsalicylic acid however resulted in larger amounts of CPM reagent present in the
products. Tartaric acid and sorbitol caused a complete inhibition of ZM production even at low concentrations.
5.4 REFERENCES


15. Zhou, Z. H.; Deng, Y. F.; Cao, Z. X.; Zhang, R. H.; Chow, Y. L., Dimeric dioxomolybdenum(VI) and oxomolybdenum(V) complexes with citrate at very low pH and neutral conditions. Inorganic Chemistry 2005, 44, (20), 6912.


18. Zhou, Z. H.; Wan, H. L.; Tsai, K. R., Bidentate citrate with free terminal carboxyl groups, syntheses and characterization of citrato oxomolybdate(VI) and oxotungstate(VI), Delta/Lambda-Na₂ MO₂(H₂cit)₂ center dot 3H₂O (M = Mo or W). Journal of the Chemical Society-Dalton Transactions 1999, (24), 4289.


25. Muller, A.; Das, S. K.; Fedin, V. P.; Krickemeyer, E.; Beugholt, C.; Bogge, H.; Schmidtmann, M.; Hauptfleisch, B., Rapid and simple isolation of the crystalline molybdenum-blue compounds with discrete and linked nanosized ring-shaped anions: Na-15 (Mo₁₂₆Mo₂₈O₄₆₂H₁₄)-Mo-VI-O-V(H₂O)₇₀ (0.5) (MO₁₂₄MO₂₇O₄₅₇H₁₄)-M-VI-O-V(H₂O)₆₈ (0.5) center dot ca. 400 H₂O and Na-22 (Mo₁₁₃Mo₂₈O₄₄₂H₁₄)-Mo-VI-O-V(H₂O)₅₈ center dot ca. 250 H₂O. Zeitschrift Fur Anorganische Und Allgemeine Chemie 1999, 625, (7), 1187.


Chapter 6

The Influence of Additives on the Seeding of

Zirconium Molybdate Synthesis
6 THE INFLUENCE OF ADDITIVES ON THE SEEDING ON ZIRCONIUM MOLYBDATE SYNTHESIS

6.1 INTRODUCTION

The formation of ZM in HALES occurs during the periods when the HAL acidity is low, which is before volume reduction and after WAR takes place.\(^1\) The volume reduction of HAL causes a temporary increase in nitric acid concentration to a maximum of around 12 molar before water-acid reduction (Section 1.2.3) reduces it back to between 2 - 4 molar. This makes the conditions under which ZM crystallizes in HALES different from the one-pot method used throughout this thesis. One of the main differences is the presence of pre-formed ZM crystals in the system when ZM synthesis begins. The ZM crystals which have formed before volume reduction have the potential to act as seed material for any subsequent ZM crystal growth after volume reduction. Seeded growth of ZM crystals is potentially very different to unseeded ZM synthesis because the growth of existing ZM crystals is known to occur much faster than nucleation of new crystals (Section 3.2.1).\(^2\)

A number of ZM morphology-directing additives have been identified previously in this thesis (Chapters 4 and 5). Their effects on seeded ZM synthesis are important to understand because the final product of seeded growth is influenced by the morphology of the seed crystal providing a structure over which subsequent growth takes place. Morphology-directing additives would also have an influence on the morphology of the secondary growth on the surface of the seed crystals.
6.2 RESULTS AND DISCUSSIONS

6.2.1 SEED CRYSTAL SYNTHESIS

The potential for ZM crystals to act as seeds for secondary ZM growth was investigated using the method described in section 2.3.6. A typical ZM synthesis was supplemented with pre-synthesised ZM seed crystals. The seed crystals were synthesised in large batches and then washed and dried until they were added to ZM syntheses reactions before the reagents.

The seed crystals used throughout this chapter were synthesised in batches large enough to supply the seed material for all the experiments in which that type of seed material was used. The use of seed material from a single source ensured that the crystals were uniform across all experiments in which they were used. This was achieved by scaling-up a typical ZM synthesis 20 times by using the method stated in section 2.3.5. These large scale syntheses achieved a yield of 60 – 80 grams of ZM using a two litre flask and a reaction time of several days. The scale-up produced ZM crystals which were larger than the crystals produced in the 100 ml flasks typically used (Figure 6.1). The average width of the crystals increased almost five-fold from 1.7 μm to 8.3 μm (Table 6-1). The size difference presented problems with regard to the continuity of the experimental system however, it allowed the easy differentiation of the seed crystals and any new ZM growth in the product which made identification of secondary growth clear-cut.
Figure 6.1 SEM micrographs of the ZM crystals. A = ZM crystals produced using a large scale synthesis method for use in seeding experiments. B = ZM crystal produced in a typical synthesis.

<table>
<thead>
<tr>
<th>Crystal Identity</th>
<th>Average Dimensions (μm x μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZM (regular)</td>
<td>1.8 x 1.6</td>
</tr>
<tr>
<td>ZM (large scale)</td>
<td>8.7 x 7.7</td>
</tr>
</tbody>
</table>

Table 6-1 A summary of the effects of large scale production on the size of the product crystals and therefore, the size of the crystals used as seeding material during ZM syntheses.
6.2.2 ZIRCONIUM MOLYBDATE AS SEED MATERIAL

The result of seeding a ZM synthesis reaction with pre-synthesised cuboidal ZM crystals (Figure 6.1A) as described in section 2.3.6 can be seen in figure 6.2. The images show that the cuboidal crystal habit of the seed crystals was preserved. Growth was seen to have occurred on the surface of the seed crystals because there was a 15% increase in the average size of the crystals before and after synthesis from 8.3 μm to 9.6 μm (Table 6.2). New crystal growth was identified as the smaller crystals visible in the images (Figure 6.2) but the new growth crystals were generally more than three times the size expected for ZM crystals and were possibly the result of secondary nuclei produced by seed crystal collisions. Overall the results showed that secondary growth occurred on ZM seed crystals and supported the hypothesis of secondary growth occurring preferentially over the formation of new nuclei.²

Figure 6.2 SEM micrographs of the product of ZM synthesis seeded with pre-formed ZM crystals
Table 6-2  A summary of the change in size of the seed crystals as a result of secondary growth during ZM synthesis.

<table>
<thead>
<tr>
<th>Crystal Identity</th>
<th>Average Dimensions (µm x µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZM (seed)</td>
<td>8.7 x 7.7</td>
</tr>
<tr>
<td>ZM (post-reaction)</td>
<td>9.8 x 9.3</td>
</tr>
</tbody>
</table>

6.2.3  SEEDING WITH ADDITIVE-INFLUENCED ZIRCONIUM MOLYBDATE

Following the results in section 6.2.2, investigations into the seeding of ZM synthesis was extended to include the use of crystals with non-equilibrium morphologies as seed material. The products of the most effective ZM morphology-directing additives were chosen as seeds for this work, the crystals formed in the presence of Te$^{6+}$ at 6 mol % (ZMT) and citric acid at 10 mol % (ZMCA) (Figures 6.3 and 6.5 respectively). ZMCA crystals had a morphology which resembled that of a square-based prism elongated along the [001] axis. ZMT crystals had a “wheat-sheaf” morphology, again elongated along the [001] axis but with divergent termini. Further explanation of the effects of the additives is contained in chapters four and five.

6.2.3.1  SEEDING WITH ZMT CRYSTALS

ZMT crystals were used as seed material in a typical ZM synthesis reaction. The experiment was performed using the method described in section 2.3.8 and the results can be seen in figure 6.4. Examination of the results revealed that secondary crystal growth occurred on all seed crystals and that the new growth overgrew the rough and irregular wheat-sheaf morphology of the ZMT seed crystals. The images revealed that secondary growth smoothed the surfaces of the ZMT crystals and caused development of the (100), (010), and (001) crystal faces known to be prominent in the control ZM crystals (Section 3.2.3.1). Overgrowth occurred on all ZMT crystals but the seed
crystals were still visible between the overgrowths in some places. The overgrowth covered the rough faces of the seed crystals making the product appear more regular, changing the rough, irregular morphology of the wheat-sheaf ZMT seed crystals into a crystal which resembled a more regular elongated cuboid. The elongation present in the ZMT seed crystals was maintained in the product crystals, indicating that some of the seed crystal character was retained in the final product and possibly decreasing the amount of additive required to obtain a certain elongation.

Figure 6.3 SEM micrograph of ZMT seed crystals pre-synthesised in the presence of telluric$^\text{VI}$ acid (5 mol%).
Figure 6.4 SEM micrographs of the product of ZM synthesis seeded with pre-formed ZMT. Images show the overgrowth of new material on the seeds causing the crystals to become increasingly regular and possibly smoother surfaces. The low energy (100), (010) and (001) faces can be seen becoming prevalent.
6.2.3.2 Seeding with ZMCA

The result of using ZMCA crystals (Figure 6.5) as seed material can be seen in figure 6.6. There was no distinct difference in the morphology of the product crystals and the seed crystals however, the product did not contain cuboidal ZM crystals known to form in an additive-free system. This result suggested that secondary growth occurred only on the seed crystals and that it was the only ZM growth to occur. The secondary growth was not obvious because the seed crystals had a square-prism morphology meaning that the low energy (100), (010), and (001) crystal faces were already established. The only difference in the product morphology from the original ZMCA seeds was the loss of the central grain boundary, a feature of citric acid additive influenced growth, in most instances overgrowth covered the central grain boundary.
Figure 6.5 SEM micrograph of the ZMCA seed crystals pre-synthesised in the presence of citric acid (10 mol %)

Figure 6.6 SEM micrographs of the product of ZM synthesis seeded with pre-formed ZMCA crystals. Images show the overgrowth covered the central grain boundary and that the elongation of the seed crystal remained in the product.
6.2.4 SEEDING IN CONJUNCTION WITH THE USE OF ADDITIVES

The work in sections 6.2.1 and 6.2.2 has shown the ability of secondary growth to occur on ZM crystals with varying morphologies. These results provided evidence that seeding in HALES would be likely to occur therefore, it is possible that secondary growth of ZM could be made to occur in the presence of one or more morphology directing additives. At any point during ZM synthesis morphology-directing additives could be introduced to the HAL causing any subsequent ZM growth to be altered. Therefore, investigations into seeding were extended to include the seeding of ZM syntheses in the presence of Te$^{6+}$ and citric acid additives.

6.2.4.1 TELLURIC(VI) ACID ADDITIVE INFLUENCE ON SEEDED ZIRCONIUM MOYBDATE SYNTHESIS

Experiments were carried out using the method given in section 2.3.7, which described the addition of cuboidal control ZM crystals (as seed material) and telluric(VI) acid at the start of the reaction. An overview of the effect of Te$^{6+}$ on ZM crystal growth can be found in section 4.2.2.

The dominant product of telluric(VI) acid addition to seeded ZM synthesis was bunches of aligned acicular ZM crystals (Figure 6.7). The reason for the bunching of the crystals became apparent when more complete products were imaged. Figure 6.8 shows acicular ZM crystals growing out from the surface of the seed crystals but only from two crystal faces (Figure 6.9). The unattached bunches of aligned ZM crystals, which made up the majority if the product, were probably grown in this way but the fragile nature of acicular crystals meant that they became detached. SAED revealed the acicular secondary growths were ZM crystals elongated along the [001] axis, the same axis of elongation observed during unseeded synthesis of ZM in the presence of Te$^{6+}$. 

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The cuboidal seed crystals in this case possessed two large faces on opposite sides similar to an orthorhombic crystal. These large faces on ZM crystals have previously been designated as the (001) and (00\overline{1}) crystal faces (Section 3.2.1) therefore, Te\(^{6+}\) directed the secondary growth to occur preferentially at faces on the [001] axis of the seed crystals (Figure 6.10).

![SEM micrographs of the product of a ZM synthesis seeded with pre-formed ZM crystals and telluric\(^{VI}\) acid (5 mol %) additive. Images show bundles of highly acicular crystals.](image)

Figure 6.7 SEM micrographs of the product of a ZM synthesis seeded with pre-formed ZM crystals and telluric\(^{VI}\) acid (5 mol %) additive. Images show bundles of highly acicular crystals.
Figure 6.8 SEM micrographs of the product of ZM synthesis in the presence of telluric acid (5 mol %) and seeded with pre-formed ZM crystals. Images show acicular crystals attached to the surface of ZM seed crystals. Revealing that secondary growth occurs mainly on the large "top and bottom" faces of the crystal which have previously been identified as the (001) and (001) crystal faces.
Figure 6.9 Schematic of the mechanism of formation of acicular crystal growth on specific surfaces of the orthorhombic-type ZM seed crystals.

Figure 6.10 Comparative images (Left) An SEM micrograph of seeded ZM growth in the presence of telluric\textsuperscript{VI} acid (5 mol %) (Right) a schematic image of the product.
6.2.4.2 CITRIC ACID ADDITIVE INFLUENCE ON SEEDED ZIRCONIUM MOLYBDATE SYNTHESIS

Unseeded ZM syntheses in the presence of citric acid (Section 5.2.2) produced crystals with elongated square-based prism morphologies. At low and medium citric acid concentrations the crystals were well formed however, at high concentrations the elongated crystals became thin and brittle.

The product of citric acid addition to seeded ZM synthesis is shown in figure 6.11. The seeding of ZM synthesis in the presence of citric acid produced crystals identical to products of unseeded synthesis with only the newly formed smaller crystals being present with the larger seed crystals. The new ZM crystals were not aligned or attached to the seed crystals as had been the case for seeded ZM synthesis in the presence of telluric\textsuperscript{VI} acid. Due to this result it was revealed that seeded citric acid synthesis had no effect on the product crystals, citric acid was consequently not used in any further seeding experiments.
Figure 6.11 SEM micrographs of the product of ZM synthesis in the presence of citric acid (10 mol \%\) and seeded with pre-formed ZMCA crystals. Images show growth of ZM crystals with a morphology typical of the effect of citric acid additives and therefore, the presence of seed crystals did not have an influence.
6.2.4.3 Seeding with ZMCA and ZMT Crystals in the Presence of Telluric(VI) Acid

The combination of morphology-directing additives and seeded ZM syntheses (Section 6.2.3.1) has been seen to produce products with attributes which differed from those produced by the use of either technique alone. This study was used to examine the effect of seeding an additive-influenced ZM synthesis with ZM crystals which had non-equilibrium morphologies. However, it was reasoned that employing the same morphology-directing additive to effect secondary growth which had been used to produce the seed crystals would produce no change from the morphology of the seed crystal and could be dismissed. Citric acid could also not be used as the morphology-directing additive because it has previously been shown to have no effect over secondary growth on ZM seed crystals (Section 6.2.4.2). Therefore, the only combination remaining from those previously validated in this chapter was the use of ZMCA as seed crystals for the synthesis of ZM in the presence of telluric(VI) acid. Te$^{6+}$ has been shown to cause face-dependent secondary growth along the [001] axis (Section 6.2.4.1) and therefore, has the potential to further extend the already present [001] axis elongation of ZMCA seed crystals. The predicted improvements to the setting properties of ZMCA crystals compared with cuboidal ZM could therefore, be accentuated and the effect enhanced.

The results of this experiment can be seen in figure 6.12. The product material shows acicular secondary growth on two faces of the ZMCA seed crystal along the [001] axis of the crystal. The product crystals of this reaction were often covered with crystalline debris (CPM) making the product difficult to distinguish however, close inspection revealed acicular secondary growth occurring solely on the terminal crystals faces, which in the case of ZMCA are the (001) crystal faces. The secondary growth
crystals can be more easily seen in Figure 6.14 which shows other examples of the face specific acicular crystal growth. Figure 6.13 are graphics which show the effects as schematics.

Figure 6.12 SEM micrographs of the product of ZM synthesis in the presence of ZMCA seed material and telluric VI acid (5 mol %). (Left) Shows the general form of the products, which were not changed much from the seed material. (Right) Shows a close-up of the hashed area selected in the left hand image. Close-up reveals directed growth on the surface of the seed crystals, similar to that reported for orthorhombic ZM.

Figure 6.13 Schematic diagram of ZM synthesis containing ZMCA seed crystals and telluric VI acid additive. The figure shows how the central grain boundary is overgrown and how the telluric VI acid directed growth forms only at the 001 crystal faces.
Figure 6.14 SEM micrographs of secondary growth on the terminal surfaces of ZMCA seed crystals. (Top) Ordered growth on the end face of the ZMCA crystal. (Bottom) Close-up of the secondary growth.
6.2.4.3.1 THE INFLUENCE OF TELLURIC\textsuperscript{VI} ACID CONCENTRATION

The concentration of telluric\textsuperscript{VI} acid additive had an effect on the size of the acicular secondary growth protruding from the (001) face of the ZMCA seed crystal (Table 6-3). At 2.5 mol % the additive had little effect (Figure 6.15A) however, the largest protrusions were produced by 5 mol % telluric\textsuperscript{VI} acid (Figure 6.15B). At higher concentrations the protrusions became increasingly small and fine (Figure 6.15C / D).

![Figure 6.15 SEM micrographs of the products of ZM syntheses undertaken in the presence of ZMCA seed crystals and various amounts of telluric\textsuperscript{VI} acid additive. A = 2.5 mol %, B = 5 mol %, C = 7.5 mol % and D = 10 mol % telluric\textsuperscript{VI} acid additives.](image-url)
<table>
<thead>
<tr>
<th>Amount of telluric\textsuperscript{VI} acid (mol %)</th>
<th>Average Length of Protrusion ((\mu\text{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>n/a</td>
</tr>
<tr>
<td>5.0</td>
<td>1.9</td>
</tr>
<tr>
<td>7.5</td>
<td>1.3</td>
</tr>
<tr>
<td>10.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 6-3 A summary of the average length of the protrusion of the telluric\textsuperscript{VI} acid directed secondary growth on the (001) face of ZMCA seed crystals.
6.2.4.3.2 DIFFERENT SEED CRYSTAL SIZES

A degree of control over the size of the ZMCA seed crystals was achieved by altering the size of the reaction vessel in which they were formed. The use of larger reaction vessels promoted the formation of larger crystals (Section 6.2). However, the size of the secondary growth remained dependent on telluric$^{\text{VI}}$ acid concentration even when the size of the seed crystals was changed. 5 mol % telluric$^{\text{VI}}$ acid was shown to produce the largest protrusion growth and was therefore, used for this study. A combination of these conclusions meant that the relative length of the seed (S) and the secondary new growth (N) could be controlled (Figure 6.16).

\[ S = \text{Length of seed crystal} \quad \text{and} \quad N = \text{Length of new growth} \]

Figure 6.16 Graphic describing the length of the seed crystal (S) and the length of the secondary growth (N).
Management of the S : N ratios of the product allowed the production of crystals with variety of morphologies (Figure 6.17). The largest S : N ratio was produced using a large seed crystal (Figure 6.17A), generating a crystal which had a similar morphology to the ZMCA seed. As the seed crystal size was reduced so the S : N ratio of the product decreased, allowing the new growth to have a greater effect on the morphology of the final product (Figure 6.17B). Figure 6.17C shows the product of using the smallest seed crystal the synthesis achieved crystals with an S : N ratio < 0.5. As the size of the seed crystals was decreased the morphology of the final product became increasingly influenced by the secondary telluric VI acid influenced growth. The morphology of the product crystals in this case had significantly divergent termini in a similar fashion to the ZMT crystals with wheat-sheaf morphology. It was expected that the crystals with the lower S : N ratios would have significantly different suspension and settling properties when compared to the seed crystals due to the extensive secondary growth.
Figure 6.17 SEM micrographs of the product of ZM syntheses undertaken in the presence of 5 mol % telluric acid and various sized ZMCA seed crystals. A = largest and C = smallest average ZMCA seed crystal size.
6.3 CONCLUSIONS

The seeding of ZM synthesis was considered as a method by which a more accurate understanding of the growth of ZM crystals in HALES systems. These included seeding pure ZM syntheses as well as reactions containing additives known to affect the ZM crystal morphology. The results revealed that ZM crystals provide a very good base for seeded ZM growth. When seed material was present new growth occurred almost entirely on the surfaces of the seed crystals, proving that the effects of seeding are important if ZM formation in HALES is to be fully understood. ZM crystals with additive-altered morphologies also proved equally good sites for secondary growth and demonstrated the preference for the expression of the (100), (010) and (001) faces on the product ZM. The product of seeded synthesis was also seen to adopt some of the structural features of the seed crystals, including their elongation. A finding which could be used to reduce the proposed amount of morphology-directing additive required to sufficiently affect the required outcome. The use of morphology-directing additives in seeded ZM synthesis provided some interesting products with novel and potentially useful morphologies. Telluric\textsuperscript{VI} acid promoted the formation of bunches of acicular crystals on specific faces of the seed crystals. Combination of the effect of telluric\textsuperscript{VI} acid with that of citric acid caused additional elongation of the products. The size of the seed crystals relative to the secondary growth material was found to be controllable and provided another degree of morphological influence available for seeded ZM synthesis, whilst also producing novel ZM morphologies. Overall the results included in this chapter have shown the diversity of the possible forms into which ZM crystals could be engineered.
6.4 REFERENCES


Chapter 7

Rheometry and Settling Studies
7 Rheometry and Settling Studies

7.1 Introduction

A number of solids such as zirconyl phosphates, barium/strontium nitrates, caesium phosphomolybdate, lanthanide nitrates, and zirconium molybdate (ZM) precipitate from solution throughout the volume reduction of HAL in evaporators and during later stages of the reprocessing of highly active waste at HALES, Sellafield. The presence of these solids in HAL waste streams is known to cause a number of significant challenges to the management of HAL in evaporators, storage tanks, and during the transport of HAL between these and other sites. The majority of the issues caused by the solids are a result of particle sedimentation producing settled beds of solids which are difficult to re-suspend and therefore, long lived.

HAL is a very corrosive mixture, having an average temperature of 55°C, a typical nitric acid concentration of 3 molar, and a maximum acidity which can reach in excess of 12 molar. The safe containment of HAL is a top priority at HALES due in part to the highly radioactive nature of some HAL components. However, structural failure caused by faster than predicted corrosion of HALES infrastructure by HAL has been reported. The temperature of HAL has a strong influence on the rate of corrosion; for example an increase of 8°C will cause the corrosion rate to increase by 50%. Therefore, controlling the temperature of HAL is important to prevent unnecessary corrosion. Evaporators and storage tanks are cooled or heated as required by external water-filled jackets and internal heat-exchange pipework. Significantly, the faster than predicted corrosion rates found at the bottom of vessels were thought in part to be caused by the presence of long-lived settled beds of solids in HAL, creating a localized increase in the temperature. The inhomogeneity recorded in HAL temperature is thought
to be partly a result of settled solids acting as an insulating layer on the base of the vessels reducing the effectiveness of the temperature control process leading to an increased corrosion rate. Another cause of settled solid induced temperature distribution inhomogeneity is the presence of heat-producing radioisotopes at high concentrations within the settled solids. HAL contains many radioisotopes and crystallization increases the corrosion rate by, concentrating and localizing any heat produced to the bottom of the vessels. There is currently no system in place which adequately agitates the liquor in HALES vessels to prevent sedimentation of the faster settling solids or re-suspend any solids which have formed stable settled beds. Although ZM does not contain any radioisotopes it contributes to the stability of the settled beds and therefore any changes to the rate of ZM sedimentation and the stability of any settled beds of ZM would influence the overall stability of HAL solids.

Sedimentation of solids will also affect the transport of post-evaporator HAL to the storage tanks or the vitrification plant at Sellafield. Many of the transfer-pipes in HALES are complex and gravity fed (Figure 7.1) therefore, the blockage of pipes by the build-up of solids at low gradient sections is a designed-in problem of HALES infrastructure. Decreasing the stability of settled beds of solids and reducing the rate of solids sedimentation would reduce solid build-up in transfer pipes.

The stability of gravity settled sediment beds and the rate of sedimentation are determined by a number of factors including particle size, solid volume fraction, particle-particle interactions, morphology of the particles, polydispersity, viscosity of the liquid medium, and settling time. The rate of sedimentation is also affected by Brownian motion of the particles although; at the size range in question Brownian motion has no influence. The concentrations of the solids in suspension have an influence on which property has greater influence. In medium and high solid volume
fraction suspensions, particle-particle interactions are the most influential forces however, they have no effect in a dilute suspension. This is because particles are often far apart at low volume fractions and have no influence over each other, meaning that the size and morphology of the particles have a greater influence on the settling rate. Alteration of one or more of the factors mentioned would result in a change to the forces required to re-suspend settled beds or the forces governing the settling rate of the solid. This would in turn affect the probability of the creation of long-lived stable settled beds and possibly aid HAL solids management.

Figure 7.1 Stainless steel HAL transfer pipework in a HAL cell
During the course of this work ZM has been synthesised using a number of different techniques and the crystals produced have a range of different features (Chapters 3 – 6). With regard to the formation of settled beds of solids in HAL the most relevant of these alterations to ZM were changes to the morphology of the crystals caused by the use of additives. The most effective additives trialled include 6 mol % Te\(^{6+}\) which caused the formation of ZM crystals with wheat-sheaf morphology (ZMT) and 10 mol % citric acid which resulted in the synthesis of ZM crystals with elongated cuboidal morphology (ZMCA). The morphology of the particles have a strong influence on both settled bed stability and sedimentation rate and therefore, these alteration could provide partial solutions to the associated problems of HAL solid sedimentation.

It is prudent to note that in addition to the alteration of the overall shape of ZM crystals through the use of additives there would have also been some changes to the size and polydispersity of the crystals. An increase in the polydispersity of a sample decreases the force required to re-suspend the solids and an increased average size will lead to a lower overall suspension viscosity.\(^{164}\) The ZMT crystals possess an increased asymmetry compared to the relatively symmetrical cuboidal ZM crystals. Asymmetry causes the viscosity of a sediment to be considerably increased upon application of small forces, a result of enhanced interparticle interactions, solvent immobilization, and disturbance of the flow of the medium.\(^{165}\) A significant increase in the aspect ratio of particles often produces a settled bed with a lower solid volume fraction caused by more open particulate packing. A lower volume fraction would result in a lower solid density and could therefore, decrease the force required to re-suspend a settled bed.
A theoretical study revealed a link between the aspect ratio of particles in a sample and the maximum random packing density of a settled bed. The study determined that ellipsoids with an aspect ratio of four or less have a higher packing fraction than cubes, and that above this threshold the solid volume fraction decreases linearly.\(^\text{166}\) Therefore, the elongation of a cube would increase the packing density of a settled bed, making it denser until the aspect ratio of the particles has exceeded four. These findings would back up the assumption that ZMCA and ZMT crystals would cause the formation of settled beds with a more open structure making them less stable (Table 7-1). However, the non-uniform nature of ZMCA and ZMT crystals makes their behaviour difficult to predict. The volume fractions of other randomly packed uniform shapes have been calculated but there is currently no reliable method for the prediction of irregular shape packing, in these cases experimental derivation is still recommended.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZM</td>
<td>1.1</td>
</tr>
<tr>
<td>ZMCA</td>
<td>4.7</td>
</tr>
<tr>
<td>ZMT</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 7-1 Comparison of the average aspect ratio of a selection of ZM, ZMCA, and ZMT crystals
7.1.1 TECHNIQUES FOR MEASURING EASE OF RE-SUSPENSION

The critical transport velocity of the sediment is a measurement of the stability of a settled bed. This is the minimum unidirectional destructive force required to re-suspend a sediment bed settled in a pipe. The method needed to determine the true critical transport velocity of a suspension requires the measurement of erosion of a settled bed of solids when exposed to a controlled flow of fluid. A test-rig for the in-situ measurement of the critical transport velocity of a suspension in small diameter pipes has previously been used to measure the critical transport velocity of HAL solids (Figure 7.2). However, this is not a standard piece of equipment and requires the use of large quantities of sample which made it impractical for use in this thesis.

![Figure 7.2 (Left) Photograph and (Right) schematic of experimental setup designed to measure the critical transport velocity of a sediment in a pipe](image)

A rotational rheometer is more commonly used to determine the stability of settled sediment and requires the use of small volumes of sample. A rotational rheometer has also previously been employed during research into HAL solids. Typically the stability of a bed of settled solids is determined using a rotational rheometer to measure the viscosity of sediment when a shearing force is applied. A stable settled bed will behave elastically when a force is applied to it at a shearing force below the shear yield stress point. At forces above this point it would exhibit viscous
flow behaviour as the sediment changes from a stable settled bed to a flowing slurry. It would be at this point where a sediment would be said to be re-suspended. Therefore, measurement of the shear yield stress point of settled beds of ZM, ZMT, and ZMCA crystals would allow the effect of the different morphologies on the stability of the sediment to be compared.

Previous shear yield stress point measurements of simulant HAL solid sediments were performed using a Bohlin CVO rheometer with a vane geometry attachment. The use of a vane geometry allows the shear yield stress point of a sample containing solids to be directly measured without any wall-slip or large particle effects and with only minimal disturbance of the sample. Measurements of the shear yield stress point have typically been done using a rheometer set to either constant stress mode designed to measure creep or set to rate controlled mode to measure stress. In each case the measured property is recorded until an equilibrium is reached, the control parameter was then changed and the tests repeated on new samples of the same material. This method was repeated until a range of conditions had been covered and an overview of the flow properties of the sediments was attained. However, it was thought that the application of a shear ramp with small sheer increases and short equilibration times to a single sample would be adequate to provide the necessary information to identify the shear yield stress point. This method would reduce the volume of each sample required and cut the experimental time of the study.
7.1.1.1 Technique Testing and Validation

A rotational rheometer set to measure the shear yield stress point begins with the lowest available shearing force and slowly increase until the sample exhibits flow. An equilibration time of one second and an experimental time of 20 minutes were used for these tests.

Initially samples were prepared from a sample of previously washed and dried ZM crystals, similar to those used for electron microscopy analysis, suspended in nitric acid (3 molar). This technique allowed the mass fraction of the solid to be accurately controlled, permitting direct comparison of the effect of the different morphologies of ZM. However, the results of initial trials of this method produced inconsistent results when repeated. Settling was identified as occurring during the test runs because a significant amount of time was required for the insertion of the geometry into the cup at the start of the sampling run. Figure 7.3 shows the effect of resting time on the results.

Vane geometries, like that used during these trials, were designed to measure homogeneous solutions and suspensions therefore, any settling would cause an inhomogeneity in the sample and produce inaccurate results. In attempt to solve the problem and prevent in-sample settling the mass fraction of solids in the sample was increased to a point where a homogeneous paste was formed. When this high mass fraction sample was left over short time-scales there were no signs of settling, however when tested the results remained inconsistent (Figure 7.4).
Figure 7.3 Graph showing the effect of pre-measurement delay time of the flow of suspensions of ZM crystal which had been prepared from pre-dried samples, re-hydrated prior to sampling.

Figure 7.4 Graph showing the inconsistent nature of shear profile of samples prepared from high concentrations of pre-dried samples to form a paste. Each sample was treated identically.
Examination of some early Sellafield tests of HAL simulant rheometry revealed that sample preparation involved the use of sample solids in their mother liquor. Although the samples in question were pre-settled in a centrifuge and the supernatant removed so that the required weight percent solid could be used. The supernatant was then replaced and a pre-shear applied, so that the sample was re-suspended and homogeneous prior to viscometry measurements. However, upon evaluation of the validity of this technique it was concluded that centrifugation and pre-shearing would cause the structure of suspension to be altered. The results would thereafter be less representative of settled solids present in HALES due to the altered rheological history of the sample. The need to keep the samples in their mother liquor and to not to wash and dry them pre-testing was however, identified as an important process. Therefore, to prevent settling occurring during testing the samples were left to form stable settled beds in their mother liquor before the excess supernatant was removed and the remaining stable settled bed used for testing. The results of using samples prepared in this manner were very consistent showing no signs of sample settling when left for varying times before testing (Figure 7.5). This test demonstrated the stability and homogeneity of the pre-settled sample beds however, this method did not allow control of the mass fraction of the samples. The loss of control of the mass of the solids in the sample meant that comparing the viscometry results of ZM crystals with different morphologies could not be done directly because the mass fraction of a sample has an influence on the overall viscosity and shear yield stress of settled beds. Any results obtained using this method would however, be applicable to the stability of settled beds as they would form in HALES.
Figure 7.5 Graph showing the consistency of three different samples prepared from a pre-settled bed of sample stored in mother liquor.
7.1.2 SETTLING TIME AND SETTLED BED DENSITY

The time required for ZM solids to fully sediment from suspension is an important measurement of how likely the solids are to form stable settled beds in HALES process vessels. A slower rate of settling would allow greater opportunity for the available in-tank agitation mechanisms to keep the solids suspended and prevent stable settled bed formation. It was rationally concluded that the non-standard morphology of some of the ZM crystals produced during studies into the effects of additives would have an effect on the settling characteristics of the crystals. The elongated and irregular nature of ZMCA and ZMT crystals had the potential to alter the settling rate of a suspension of the sample. A decrease in the settling rate of either ZMCA or ZMT samples would suggest that formation of that type of ZM in HAL would aid solids management by reducing the probability of long-term stable settled bed formation.

Typically settling rate measurement involves the use of very long glassware columns (~ 2.5m) and large amounts of sample (> 20 litres). However, the space and the volume of sample required made the use these techniques prohibitive. A smaller version of the equipment was instead improvised, in which 250 cm³ glass measuring cylinders were used as settling columns because they possessed uniform size, shape, and cross-section and have regular volumetric markings (Figure 7.6). The volume of sample and supernatant required to fill the equipment was also within the capabilities of the synthetic setups already in place. In each case the rate of settling was determined by measurement of the volume of the solid suspension as they settled. The settling rate was measured in this way because particles in a homogeneous solid suspension will either settle individually or form a reasonably homogeneous dispersed phase of solids in the liquid supernatant medium. The volume of the dispersed phase can be measured
because there is often a discrete boundary between the two. The rate of dispersed phase volume decrease is affected by a combination of factors including solid concentration, particle size, and the formation of aggregates. 40, 163, 164

Figure 7.6 Photograph of an improvised 250 cm³ measuring cylinder settling column. Image shows yellow settled sample at the base of the cylinder.
Initial tests of the shear yield stress point measurement set-up (Section 7.1.1.1) revealed the need for the use of samples which had not been washed and dried prior to testing to obtain reliable results. Therefore, all suspensions tested were kept in their mother liquor before settling experiments and any extra liquor required for the tests was taken from the supernatant. The need to use samples which had been kept in their mother liquor meant that the traditional method of measuring the settling of a set mass of solid could not be used because it required the solids to be dried and weighed. Therefore, a designated final settled bed volume was chosen as the best way of comparing the results of the different ZM solids. In each case the sample was introduced to the settling column before the volume of supernatant was increased to the 250 cm$^3$ mark. Sample preparation then involved the mechanical homogenisation of the solid before it was left to settle completely with no further change in the settled bed volume, this usually occurred over several days. The volume of the settled bed was then checked and sample removed or added as required to correct the volume fraction to the required amount. The homogenisation, settling, and checking process was then repeated until the sample had the required stable volume fraction. The homogenation was done using a long spatula to break-up any settled aggregates and then agitate the mixture over several minutes to suspend the crystals homogeneously throughout the length of the settling column. Effort was made not to aerate the suspension and to prevent the formation of any enduring turbulent flow or eddies.
7.2 RESULTS AND DISCUSSIONS

7.2.1 SETTLING STUDIES

A study was undertaken in which samples of ZM crystals were placed in settling columns (250 cm³) as described in section 2.2.11 and explained in section 7.1.2. In each case the solids were manually homogenised before being allowed to settle. The rate of settling was measured by recording the volume of the dispersion of solids as it decreased over time in the supernatant. The settling of three different types of ZM was tested simultaneously; cuboidal “control” ZM, elongated cuboidal ZMCA, and elongated wheat-sheaf ZMT (Figure 7.7). Three different solid volume fractions were tested for each type of ZM trialled; 7 % (dilute), 12 % (intermediate), and 24 % (concentrated), to allow greater understanding of the effects which the different morphologies have on suspension structure over a range of solid concentrations. The concentration of the concentrated volume fraction sample was chosen because it was similar that of solids found in simulant HAL experiments.40

Figure 7.7 SEM micrographs of the crystals which are present in the three different samples. A = ZM, B = ZMCA, and C = ZMT
Figure 7.8 Graphs showing the volume of the settled sediment of ZM, ZMT and ZMCA for A - 7 %, B - 12 %, and C - 24 % volume fractions.
The 7% volume fraction sample produced results which suggested that at dilute concentrations there was no difference in the behaviour of the ZM and ZMCA crystals but the ZMT sample settled significantly quicker (Figure 7.8A). The tendency was that the solid dispersion volumes decreased quickly over the first 15 minutes (6.1% min\(^{-1}\) for ZMCA), in which time the majority of settling had taken place. However, the rate of settling for ZMT during the first 10 minutes was 12.7% min\(^{-1}\), double the rate of ZM and ZMCA. The rate then slowed and after 15 minutes the settling rates for all three samples were very similar and much slower than the initial rates. The dilute nature of these samples meant that the particles would not come into contact during the initial stages of sedimentation and implied that the early rate of settling recorded was representative of the settling of individual particles. Concentration of the particles during this time caused the particles to begin interacting with each other, and resulted in some particle aggregation and the formation of a settled bed. A sample has a settled bed when all suspended solids are into contact with each other and in the case of these results was responsible for the abrupt settling rate decrease after 15 minutes for all samples. The formation of a settled bed changed the mechanism of settling from one concerning individual particles to what is called hindered settling, which occurs when further settling can only progress by the action of the supernatant being squeezed from between the particles or aggregates as the weight of the upper settled solids cannot be supported by the lower extended aggregate structures and aggregate networks, which breakdown under the applied stress.\(^{165}\) Hindered settling is a slower mechanism of settling than that of individual particles because it relies on extended aggregate network strength and the release of captured supernatant.

Results for the 12% volume fraction sample indicated that ZMT and ZMCA settled at much the same rates and that ZM was marginally the slowest settling of the
three (Figure 7.8B). The intermediate concentration results revealed two discrete trends in the rate of solid settling. After a short delay ZMCA and ZMT began to settle at a rate of 2.2 % min$^{-1}$ until the solids had settled to under half their original volume. At this point the rate of settling decreased abruptly, slowing to 0.05 % min$^{-1}$, a rate which slowly decreased until settling had been completed. The settling of ZM followed a very similar profile but the initial delay before settling began was almost twice as long as that of ZMCA and ZMT. The delay seen for all samples at the start of settling can be attributed to the re-orientation of the randomly distributed particles to the direction of flow. The higher concentration of particles in the intermediate sample increased the interparticle interactions and allowed aggregates to form. The slower initial rate of settling prior to settled bed formation, when compared to the dilute experiment was caused by the higher viscosity of a sample with a larger volume fraction of the suspension. The fractal-like structure of aggregates caused them to occupy more space than individual particles and made the volume of the settled bed greater than that for individual particles.

The 24 % volume fraction sample showed a significantly different settling profile to the dilute and intermediate concentration studies (Figure 7.8C). After a significantly long delay (10 minutes for ZM and 60 minutes for ZMCA and ZMT) the solids began to settle, slowly at first then increasing to a maximum rate after 100-200 minutes. ZM was the first sample to begin visible settling and once settling had begun it occurred faster for ZM than either ZMCA or ZMT. Samples of ZMCA and ZMT took six times longer than ZM to visibly start settling and once settling had started both rates of settling were very similar up to three hours (ZMCA = 0.12 %, ZMT = 0.11 % min$^{-1}$). After three hours the rate of ZMT settling slowed to 0.03 % min$^{-1}$ and the rate of ZMCA settling increased slightly to 0.13 % min$^{-1}$. The rate of ZMT settling remained at the
same rate until two days had passed, at which point it slowed gradually until 4 days when the majority of the settling had occurred. The slight increase in the settling rate of ZMCA after 3 hours lasted for a further 2 hours, and then gradually slowed for the remainder of the experiment. After three days the solid volume fraction of each sample was roughly equal. The long delay encountered before settling began and the slow settling experienced throughout was a result of the high solid concentration causing immediate formation of large particulate aggregates. The aggregation of solids produced a settled bed instantly at the start of the settling experiment because the sample had a high solid volume fraction. Settling then took place through a hindered settling mechanism which continuing until all the solids were fully settled.

Measurements showed that once formed the volume of ZMT settled beds decreased slower than the others (Figure 7.8B/C) and that ZM aggregate settled beds broke down quicker than those of ZMCA and ZMT, undergoing hindered settling more easily. Investigation of the density of the settled beds after the settling experiments had been completed provided explanation of the slow settling of ZMT settled beds. Although the volume fraction of the samples was the same, when the density of the settled beds was calculated using the method described in section 2.2.12, the result revealed that ZMT settled beds were almost twice as dense as those of ZM (Table 7-2). Revealing that ZMT crystals were more tightly packed in the stable settled bed. This could have been an effect of the smaller size of the crystals. Denser settled beds experience slower hindered settling due to the formation of stronger aggregate networks which undergo slower breakdown and slower supernatant release. The greater final stable settled bed density of ZMT was explained by consideration of the average size of the particles, $112 \, \mu m^3$, which was roughly a fifth that of either ZM or ZMCA allowing closer particle packing and a higher solid density.
7.2.2 Settled Bed Density Comparison

The greater density of both ZMCA and ZMT settled beds when compared to ZM was not predicted. It was thought that the elongated cuboid or wheat-sheaf morphologies of ZMCA and ZMT respectively would have caused a more open settled bed packing and a lower density. However, the open packing of ZMCA was more evident during hindered settling because it caused the rate of settling to be significantly slower than ZM at similar settled bed densities.

Attempt was made to compare the settling profile of the samples taking into account the density of ZM, ZMCA, and ZMT (Figure 7.9). The settling plots were taken from the volume fraction measurements and combined in a way which allowed comparisons of the settling rates and sample densities to be drawn. The graph showed how at similar mass fractions the rate of ZMT settling was significantly quicker than those of ZM and ZMCA, providing a confliction with the conclusions of the volume fraction tests. The graph also show how much more stable ZMCA settled beds were relative to both ZM and ZMT and the difference in final settled bed volume of the different samples with similar mass fractions. The use of mass fraction based settling rate comparison but could be a more useful measure of ZM settling rates industrially.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g cm(^{-3}))</th>
<th>Average Particle Size (µm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZM (Cuboidal)</td>
<td>0.227</td>
<td>531 (±5)</td>
</tr>
<tr>
<td>ZMCA (Elongated cuboidal)</td>
<td>0.256</td>
<td>529 (±3)</td>
</tr>
<tr>
<td>ZMT (Wheat-sheaf)</td>
<td>0.431</td>
<td>112 (±15)</td>
</tr>
</tbody>
</table>

Table 7-2 Densities of settled beds and average size of the different types of ZM crystals
Figure 7.9 A graph showing the settling profile of samples of ZM, ZMCA, and ZMT with similar mass fractions (w/w). A comparison not possible before settling because the densities of the various samples was not known.
7.2.3 RHEOMETRY

The viscometry profile of samples of ZM solids were measured against a slowly increasing shearing force as described in section 2.2.10 and rationalised in section 7.2.1. The samples used were stable settled beds of ZM solids stored in the liquid medium in which they were synthesised. The viscosity of the samples was measured using a Bohlin CVO rheometer fitted with a vane geometry attached, to apply a shearing force which increased on a logarithmic scale from 0.0124 Pa to a maximum of 15 Pa over a time of 20 minutes. The samples tested included control ZM formed in the presence of no additives and possessing a morphology which resembled that of the crystals thought to form in HAL. The other samples were ZM synthesised in the presence of two morphology-directing additives, citric acid (ZMCA) or Te$^{6+}$ (ZMT), the morphology of which can be seen in figure 7.7.

![Graph showing the viscosity of ZM, ZMCA, and ZMT when a ramped shear stress was applied.](image)
Comparison of the results of the three samples (ZM, ZMCA, and ZMT) revealed that each possessed a similar but distinctly different viscosity profile in response to the applied shearing force (Figure 7.10). The viscosity profile of the ZM sample (Figure 7.11) contained a number of features which were repeated in the profiles of both ZMCA and ZMT and will herein be explained and used as a reference for the other samples. Initially the ZM rheometry measurements revealed a relatively constant viscosity during the application of an increasing shearing force (Figure 7.11A). The momentary increases and decreases in viscosity during this period were a result of the re-orientation of the initially randomly distributed aggregate particles and extended aggregate networks. Realignment of the aggregates and aggregate structures with the direction of the shearing force was considered internal particulate readjustment but not particulate flow. The stable viscosity state continued until point B on the graph where the viscosity rapidly dropped, a processes termed shear-thinning, this point represented the shear yield stress point (Figure 7.11B). The decrease in viscosity at this point was a result of the extended networks of the ZM aggregates aligned during the low shear phase breaking into individual aggregates. The breakdown of the extended aggregate structure reduced the viscosity of the sample and allowed some particulate flow to occur. The shear-thinning was then halted and a second viscosity plateau formed, which was a result of the resistance to flow of the individual ZM aggregates (Figure 7.11C). As the applied shearing force continued to be increased the sample again experienced shear-thinning (Figure 7.11D), which was this time a result of the breakdown of the aggregates into individual particles. The breakdown of aggregate structure and resultant shear-thinning occurred over a shear range one thousand times greater than the first period of shear thinning and was caused by the difference in size, strength, and complexity of the different types of aggregate compared with the loose association of
particles in the extended aggregate network (Figure 7.11E). The shear-thinning stopped when all aggregate character had been broken down and particulate flow began to occur unhindered, allowing the sample began to behave like a Newtonian fluid (Figure 7.11F).

![Graph showing the viscosity a sample of cuboidal zirconium molybdate “ZM” when a ramped shear stress was applied.](image)

**Figure 7.11** Graph showing the viscosity a sample of cuboidal zirconium molybdate “ZM” when a ramped shear stress was applied.
The viscosity profile of ZMT exhibited all of the same features as ZM (Figure 7.10); it possessed two viscosity plateaux connected by two periods of shear-thinning. The difference between the two samples was that ZMT had an initial viscosity three times higher and a shear yield stress point at over twice the shear of ZM. The increased viscosity and higher shear yield stress point was attributed to the ZMT sample having a density almost twice that of ZM (Table 7-2). The increased number of particles present would have caused more particle-particle collisions and therefore, a greater resistance to flow and a higher viscosity.\textsuperscript{168, 169} The similar form of the ZM and ZMT viscosity profiles revealed that the two samples followed the same structural breakdown processes during measurement. However, the higher density of ZMT caused the breakdown of the extended networks and aggregates to require more force than for the ZM and ZMCA samples. This result backs up the finding of the ZMT settling rate study which exhibited the slowest settling of the samples tested (Section 7.2.1, Figure 7.8C).

The profile of ZMCA initially followed a very similar trend to that of ZM, presenting very similar viscosities during low shear stresses, although the shear yield stress point of ZMCA was slightly lower than that of ZM (Figure 7.10). However, the most notable difference in viscosity profiles occurred at a shearing force of 3.75 Pa when the viscosity of ZMCA increased by over $10^5$ times, rapidly reaching $3.9 \times 10^6$ Pas at its maximum. An increase of viscosity during the application of a shearing force is termed shear-thickening and in this case was thought to be caused by hydrodynamic jamming of the sample, a result of the low polydispersity and elongated-cuboidal or rod-like morphology of ZMCA crystals. The low polydispersity of the particles caused the space between the particles to be less than in a relative sample with an equal volume fraction but a higher polydispersity. The rod-like morphology of ZMCA crystals meant that they would be expected to align with the direction of the shearing force, so as to
offer least resistance during lower shears. This alignment and the small amounts of space between the ZMCA crystals were responsible for the hydrodynamic jamming because the application of a shearing force above a certain shear rate would cause the ZMCA rods to begin to rotate about their centre, causing them to collide with each other (Figure 7.12). The result was the formation of a "logjam" in the sample, where plugs of rigid particles block the flow of the system, resulting in instantaneous increased sample viscosity.

Figure 7.12 Schematic of the mechanism which causes shear-thickening in ZMCA settled beds when a shearing force is applied. Large straight arrows show the direction of shearing force, small straight arrows represent motion of the particles, and small curved arrows represent rotation.
7.3 CONCLUSIONS

Examination of the effect of ZM crystal morphology on some important properties of sample suspensions revealed an encouraging relationship. The tests undertaken were designed to gauge the probability of ZM solids with different morphologies forming long-lived stable settled beds. Investigation into the rate of settling revealed that the concentration of the solids and the particle morphology had a strong influence on the results. At low concentrations the particles behaved like individual particles and the differences between the results were small. However, at higher concentrations interparticle collisions and aggregate network formation became increasingly influential. ZMCA formed very stable settled beds which proved to be more stable than those of ZM and ZMT at similar mass fractions. The large volume of particle aggregates effected the volume at which stable settled beds formed and therefore, because elongated structures tend to form aggregates with larger volumes the settled beds were slower to compact. Once formed, the settled beds of ZMT and ZMCA in the higher concentration samples lasted significantly longer than those composed of the cuboidal ZM. The settling of ZMT and ZMCA took almost ten times as long to reach the same volume of cuboidal ZM. The final density of ZMCA and more notably ZMT settled beds were greater than that of cuboidal ZM which also affected the rate of hindered settling. The reason was that the greater density meant that more ZMT and ZMCA particles were present and that more inter-particle interactions would occur during settling therefore, making the sample more viscous and slowing settling.

The stability of settled beds once formed was another important property of solid-liquid mixtures which was investigated by measurement of the force required to re-suspend a stable settled bed of a sample. The measurements were done using a rotational rheometer set to apply a slowly increasing shearing force to a stable settled
bed of sample with a vane geometry attachment. The viscosity and the point at which the behaviour of the samples changed from that of an elastic solid to a flowing suspension, the shear yield stress point, were then recorded. Results revealed that sample density and particle morphology were both important factors in the reaction of different samples to application of a shearing force. ZMT settled beds had the highest viscosity and shear yield stress point which was over twice that of ZM. However, ZMCA reacted very similarly to ZM but at high shearing rates underwent a sudden period of high viscosity caused by hydrodynamic jamming.

Overall, the changes made to the morphology of ZM crystals, in the form of ZMCA and ZMT produced suspensions with vastly different settling rates at the higher volume fractions. However, once sedimentation had occurred ZMCA and ZMT settled beds were generally more difficult to re-suspend than cuboidal control ZM. Industrially the slower rate of ZMCA and ZMT settled bed compression over the short time scale would allow more chance for the solids to stay suspended because the formation of stable beds over a longer time would cause them to have lower densities for longer.
7.4 REFERENCES


Chapter 8

Conclusions and Future Directions
8 CONCLUSIONS AND FUTURE DIRECTIONS

8.1 GENERAL CONCLUSIONS

In this thesis it was shown that the synthesis of zirconium molybdate for any future research into nuclear waste reprocessing should be undertaken using a two-step method involving the use of caesium phosphomolybdate (CPM) and pre-conditioned zirconyl nitrate solution as reagents. Calculations of the rate of zirconium molybdate precipitation during this synthesis revealed it to be roughly first order, limited by the rate of molybdate release from the CPM reagent. A novel method of zirconium molybdate synthesis was also presented which was analogous to the above method but which produced an uncontaminated product. This method substituted CPM for phosphomolybdic acid (PMA), a reagent used in the production of CPM. An exchange which allowed greater control of the rate at which zirconium molybdate was produced which also provided some control over the morphology of the product crystals. A faster rate of synthesis produced zirconium molybdate crystals which were elongated along the [001] axis, whereas a slower rate of synthesis generated more cuboidal crystals. This control was the result of the higher number of attachment sites available at the (001) crystal faces compared to the (100) and (010) faces.

The effect of some of the more abundant inorganic components of highly active liquor (HAL), in which zirconium molybdate grows industrially, as additives to a stand-alone synthesis of zirconium molybdate was tested. The results revealed that of the elements trialled only tellurium, probably as Te\(^{6+}\), had any influence on the growth and subsequent morphology of zirconium molybdate. Producing crystals with a range of morphologies including elongated cubes and wheat-sheaves. The addition of some selected organic molecules, not present in HAL but known to complex molybdate
species, was then trialled. A number of these caused the rate of zirconium molybdate synthesis and morphology of the product to be affected. The most effective morphology altering organic additives trialled was citric acid, which produced crystals with over eight times the aspect ratio of control crystals without causing retardation of the growth rate. Another organic additive of note was acetylsalicylic acid which caused a massive reaction rate increase during the early stages of the reaction at low additive concentrations. The direction of elongation for all of the additive influenced crystals was again along the [001] axis. A mechanism was produced to explain the axis of elongation and morphology of the zirconium molybdate crystals produced in the presence of citric acid.

The possibility of seeding during zirconium molybdate formation in HAL was identified and its effects were examined including the use of morphology-directing additives in some cases. The products included ZM with several novel morphologies produced by developing the use of one or both of the more effective additives; Te$^{6+}$ or citric acid. The use of Te$^{6+}$ resulted in the formation of face-specific growth of acicular zirconium molybdate crystals on the seed crystals. That effect was also used to produce an exaggeration of the elongation axis of citric acid elongated crystals, an effect which was shown to be controllable. The results also suggested that seeding could be used to reduce the amount of additive required to have an effect on crystal morphology.

Rheological testing on a small variety of ZM crystals with different morphologies caused by the addition of individual additives proved the hypothesis that altering the morphology of ZM crystals via changing the environment in which they were grown was able to significantly alter their behaviour in suspension and settled solids. The results revealed that both the settling rate and stability of the settled beds of solids were effected. The changes in behaviour coming from additive induced alteration
of particle size and morphology. These factors altered the mass fraction of the samples and resulted in slower hindered settling caused by greater aggregate structure stability and higher suspension viscosity compared to a control sample.
8.2 FURTHER RESEARCH

8.2.1 WORK NEEDED TO MAKE THIS RESEARCH APPLICABLE TO INDUSTRY

The work contained within this thesis has covered and in most cases exceeded all of the tasks and queries presented when the work was planned. A wide variety of techniques and ideas were brought together to produce results which went some way to providing techniques which could be used to aid the management of solids known to form in HAL. The techniques used were proven to affect the settling, re-suspension, and settled bed density of zirconium molybdate solids and therein reduce the risk of hot-spot formation and transfer-pipe blockage, two of the major challenges facing HAL solids management. However, these findings were made using batch preparation on a small scale in an ideal environment and therefore, the result did not necessarily accurately reflect the way zirconium molybdate would respond in real HAL. To make the findings more applicable to industrial conditions the tests would have to be repeated in a scaled-up batch containing some of the major components of HAL. If the effect remained and the settling and rheology of the solid suspensions were improved, the technique would have to be further scaled up and a full simulant batch containing all species known to be present in HAL would be run. The methods used during the full simulant batch would mimic the processing of HAL to make the results as accurate as possible. The solids and liquids making up the product would then have to be fully characterized and compared with a control sample and various elemental concentration ranges designed to keep the processing of HAL within operational limits. If the tests still provided improved outcomes, the changes to the composition of HAL on the downstream processes would have to be tested. This would take place at the Sellafield vitrification test rig and would be used to judge the effect on HAL vitrification. Only after these tests had been completed could a change to the processing of HAL could be put into operation.
8.2.2 RECOMMENDATIONS FOR APPLICATION OF FINDINGS

8.2.2.1 SETTLING

The industrially significant aspects of this work were concerned with the sedimentation and re-suspension properties of large volumes of precipitated solids. A brief investigation of these properties was included in this thesis. This investigation was designed to be a preliminary study, aimed to prove conceptually that the technique worked and provided the required results. The systems required to test the effects of the techniques fully, in a way which would make them applicable to actual process application, would require extensive experimental set-ups, large quantities of test material, and long term runs. All of those aspects meant that it was impracticable to attempt to undertake them during this PhD. However, there are some facilities and equipment present at the national nuclear laboratory site at Workington which have been designed specifically to test these properties and could be used.

8.2.2.2 ADDITIVES

Further tests on the effect of untested additives and more specifically combining multiple additives would allow greater understanding of the effects of an additive species on zirconium molybdate growth in HAL. It would also allow the formulation of a method for predicting the morphology of zirconium molybdate in industrial HAL batches through consideration of the components of the growth liquor. Combined with rheological and settling data this would potentially be very beneficial to HAL solids management because it would allow prediction of the formation of blockages and settled beds of solids. It would therefore allow any problems to be identified and addressed earlier before they cause any issues. It would also provide useful information.
when legacy wastes are assessed and allow future planning of batch feed concentration restrictions.

Assessment would also be needed of the effect of organic additives in HAL on the production of foam. To address any safety concerns regarding the potential of foam to carry radioactive material into unshielded areas. It had been suggested that the use of organic additives be carried out along with post-operative clean-out trials, because that set-up would be designed to cope with foam production.

Accurate prediction of the settling properties of all solids in HAL would require separate studies of each element present in HAL on each different solid, similar to those undertaken by zirconium molybdate. The formation and effect of any additives used would have to be trialled for each solid known to form in HAL. Only when these were complete and a system of predicting the impact of each element present in HAL on the formation and rheology of each solid could this be accurately predicted.

8.2.3 **Molecular Modelling**

Molecular modelling was employed in an attempt to better understand the changes in morphology of zirconium molybdate observed during changes to the synthetic conditions by calculating surface energies. Data was used from the original paper on zirconium molybdate crystal structure by Clearfield and an attempt was made to construct a valid potential using the GULP molecular modelling freeware. After numerous failed attempts to build the potential it was concluded that there was an inaccuracy in the published location of the water molecules. In attempt to resolve this issue an application was sent for time at a neutron diffraction facility so that the water
molecule location could be more accurately designated. This application was rejected and the endeavour taken no further.