TRANSFORMING DENTAL MOULD WASTE (DMW) INTO HIGH PURITY CALCIUM SOURCE BY CHROMIUM REMOVAL THROUGH ALKALINE CAUSTIC LEACHING (ACL) USING ULTRASONIC TECHNOLOGY

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled Transforming Dental Mould Waste (DMW) Into High Purity Calcium Source By Chromium Removal Through Alkaline Caustic Leaching (ACL) Using Ultrasonic Technology. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

μm – Micrometre

nm – Nanometre

α – Alpha

β – Beta

γ – Gamma

° - Degree

°C – Degree celcius

kHz – Kilo hertz

% - Percentage

MPa – Mega pascal

Å – Armstrong

LIST OF ABBREVIATIONS

XRD – X-ray diffraction

XRF – X- ray fluorescence

FTIR – Fourier transform infrared

SEM – Scanning electron microscope

DTS – Diametral tensile strength

DMW – Dental mould waste

NaOH – Sodium hydroxide

Na_2CrO_3 – Sodium carbonate

Cr – Chromium

Ca – Calcium

Cr_2O_3 – Chromium oxide

CaO – Calcium oxide

MgO – Magnesium oxide

SiO_2 – Silicon dioxide

Na_2CrO_4 – Sodium chromate

$CaOH_2$ – Calcium hydoxide

$CaSO_4$ – Calcium sulfate

$CaSO_4.2H_2O$ – Calcium sulfate dihydrate

MENGUBAH SISA ACUAN PERGIGIAN (DMW) KEPADA SUMBER KALSIUM BERKETULENAN TINGGI DENGAN PEMBUANGAN KROMIUM MELALUI LARUT LESAP KAUSTIK BERAKALI (ACL) MENGGUNAKAN TEKNOLOGI ULTRASONIK

ABSTRAK

Pembuangan sisa acuan gigi (DMW) ke tapak pelupusan semakin meningkat setiap tahun dan IPPT Bertam, Pulau Pinang juga mempunyai banyak DMW yang perlu dibuang setiap bulan. Seperti yang kita sedia maklum, sisa acuan gigi dikenali sebagai gipsum dan mempunyai kandungan kalsium yang tinggi. Oleh itu, kitar semula DMW merupakan pendekatan yang mampan untuk mendapatkan sumber kalsium alternatif, yang boleh digunakan selanjutnya dalam aplikasi biokeramik. Sumber kalsium ini kemudiannya boleh digunakan sebagai prekursor utama dalam menghasilkan bioseramik akermanit. Kajian ini boleh dibahagikan kepada dua bahagian: (1) sintesis kalsium hidroksida menggunakan frekuensi berbeza teknologi ultrasonik (40, 132, 360 kHz) dengan mengeluarkan kandungan kromium dalam DMW (2) fabrikasi bioseramik akermanit menggunakan sumber kalsium daripada DMW disinter pada tiga suhu (1200,1225 dan 1250°C). Keputusan yang diperoleh menunjukkan bahawa 40kHz adalah frekuensi yang paling cekap dalam mengeluarkan kandungan kromium daripada DMW, menghasilkan ketulenan kalsium hidroksida yang lebih tinggi. Dapatan ini menyokong teori di mana frekuensi ultrasonik yang lebih rendah biasanya digunakan untuk serbuk yang lebih kasar. Sementara itu, suhu pensinteran optimum dalam menghasilkan seramik akermanit ditentukan pada 1225°C.

TRANSFORMING DENTAL MOULD WASTE (DMW) INTO HIGH PURITY CALCIUM SOURCE BY CHROMIUM REMOVAL THROUGH ALKALINE CAUSTIC LEACHING (ACL) USING ULTRASONIC TECHNOLOGY

ABSTRACT

The dumping of dental mould waste (DMW) into landfill is increasing every year and IPPT Bertam, Penang also have a lot of DMW that need to dump every month. As we know, DMW is recognised as gypsum, which has high calcium content. Thus, recycling of DMW seems as a sustainable approach to obtain alternative source of calcium, which can further be used in bioceramics applications. This calcium source can then be used as the main precursor in producing akermanite bioceramics. This study can be divided into two parts: (1) synthesis of calcium hydroxide using different frequencies of ultrasonic technology (i.e. 40, 132, 360 kHz) by removing the chromium content in DMW (2) fabrication of akermanite bioceramics using calcium source from DMW sintered at three temperatures (1200,1225 and 1250°C). The results obtained showed that 40kHz is the most efficient frequency in removing chromium content from DMW, resulting in higher purity of calcium hydroxide obtained. This finding supports the theory where lower ultrasonic frequency is commonly used for coarser powders. Meanwhile, the optimum sintering temperature in producing akermanite ceramics is determined to be at 1225°C.

CHAPTER 1

INTRODUCTION

1.1 Background

Biomaterials are materials specifically designed for a biological system for treatment, replacement, or increasing the lifetime of biological functions. Bioceramics can be classified as inorganic biomaterials that include amorphous glasses, glass ceramics and crystalline ceramics. The application of bioceramics generally provides replacement, repair and regeneration of bone and teeth however, the application is expanding into other applications nowadays (Jones *et al*., 2020). Moreover, bioceramics are specifically used as bulk materials in tissue engineering scaffolds and the replacement of grafts due to its ability to degrade in human bodies (Kiaie *et al*., 2017).

Usually, calcium phosphate and calcium silicate act as bioceramics based on medical treatment. Calcium phosphate is widely used because calcium phosphate-based has the highest similarity with bone minerals (Roy *et al*., 2017). Meanwhile, the dissolution and degradable properties of calcium-silicate based are worth it for the regeneration of bone cells (Wang *et al*., 2014). Instead of being broadly used in bioceramics calcium phosphate have its own pros and cons where even though it has ability to control injectability, porosity, mechanical properties, and degradation rate but the drawbacks are including a difference in bone regeneration and degradation rates, pore size limitations, a lack of mechanical strength, and an inflammatory reaction to synthetic polymers (Jeong *et al*., 2019). Calcium silicate also have the advantages and disadvantages, it known as good apical sealing, in presence of moisture it able to provide good setting and acquiring a high pH after mixing. Unfortunately, these materials have low followability, a dry consistency, and a lengthy setting time (Marković *et al*., 2016).

Akermanite ($Ca_2MgSi_2O_7$) also used in bioceramics for repair of bone, and it provided good degradation properties, preferable mechanical strength and bioactivity (Tavangarian *et al*., 2020). The source of raw materials been used in producing akermanite are calcium (Ca), magnesium (Mg) and silicon (Si). In producing akermanite it may involve wet and dry synthesis, dry synthesis of akermanite highly preferably and it involved high-speed planetary ball milling as it more efficient and simpler. The fabrication of akermanite through wet synthesis are ineffective for scaling up to produce large quantities of akermanite due to difficulties in regulating the crystallinity and phase purity of nanoparticles, as well as some technically complex and time-consuming procedures (Zadehnajar *et al*.,2021).

For this study, akermanite pellets are in an attempt to produce using calcium powders extracted from dental mould waste (DMW). Akermanite will continue to be used as a scaffold for body implants, and it is crucial for the formation of new bone. The new bone that wants to fabricate must follow the desired shape through biologically active development (Zare *et al*., 2016). Other than that, scaffolds that wish to use as an implant must degrade with time and promote osteogenesis. Based on a recent study, the usage of akermanite scaffolds is better than β-tricalcium phosphate as akermanite scaffolds has an abiliy to degrade faster and promote high osteogenesis (Diermann *et al*., 2019).

Dental mould waste (DMW) identified as gypsum is a naturally occurring mineral suitable for use as raw material for biomaterials. Gypsum is composed of calcium sulfate dihydrate, when heated above a temperature of 120^oC anhydrate and hemihydrate calcium sulfate will form. Moreover, Plaster of Paris is formed from gypsum, and when heated at 150^{o}C in the kiln, gypsum will lose water to form Plaster of Paris. Thus, gypsum will undergo chemical reactions (equation 1.1 and 1.2) like the following:

$$CaSO_4.2H_2O(\text{Gypsum}) \xrightarrow[\text{Heat}]{} CaSO_4.\tfrac{1}{2}H_2O\ (\text{Plaster of Paris}) + H_2O(\text{steam})\ (\text{eq. 1.1})$$

Next, rehydration occurs when the addition of water to plaster of Paris becomes hardened caused by water absorption.

$$2CaSO_4.\tfrac{1}{2}H_2O\ (\text{Plaster of Paris}) + 3H_2O \rightarrow 2CaSO_4.2H_2O\ (\text{Calcium sulfate dihydrate}) + \text{heat}\ (\text{eq 1.2})$$

1.2 Problem Statement

In the dentistry field, dental moulds are one of the widely used products that only can be used once for every patient. For the production of dental moulds, the material composition consists of gypsum, non-degradable materials. Gypsum is a kind of mineral that classifies as calcium sulfate. The compositions of materials contain calcium and the chemical formula known as calcium sulfate dihydrate ($CaSO_4.2H_2O$). Even though dental mould waste (DMW) rich in calcium sources, it still has chromium (Cr^{3+}) composition known as toxic materials. It can affect the environment and human health if the disposal of DMW is out of control (Rischo Taufik Achmad *et al.*,2017).

After being used, the dental mould waste consisting of gypsum will be disposed of and there are two methods of gypsum disposal. Gypsum can be disposed by recycling and specific landfill set up for gypsum dumping purposes (Rebecca Allen, 2016). However, when the gypsum is dumped into a landfill, it can cause pollution as hydrogen sulfide gas is produced. The hydrogen sulfide, known as toxic and flammable gas is trapped in the air for one day or longer than in the winter season. The production of this gas greatly affects human health and the environment through absorption into groundwater or releasing harmful gas into the air (Parimal Chandra Bhomick, 2014). The hydrogen sulfide gas definitely threatens human lives and threatens the quality which may affect the plantation as well.

On top of that, the most efficient frequency that suitable for the removal process of chromium (Cr^{3+}) is still in investigation as to obtain high purity of calcium ($Ca(OH)_2$). In previous study, the chromium removal through alkaline caustic leaching that conducted manually unable to remove 100% of chromium ion content but only 94% (Mohd Rosli & Baba Ismail, 2022). Thus, alkaline caustic leaching that uses ultrasonic technology with various frequencies will be conducted in this study. This leaching technique may be more effective than manual leaching as it involves vibration of ultrasonic with different frequencies. Other than that, the sintering temperature of akermanite ($Ca_2MgSi_2O_7$) pellets is being investigated and gaining the best temperature that can be used to produce sintered pellets with high densification and able to reduce defects.

1.3 Research Objectives

1) To investigate the possibility of ultrasonic technology at different frequencies (40, 132 and 360 kHz) and temperatures (29ºC and 39ºC) in producing pure calcium source by removing chromium ions from the dental mould waste.
2) To optimize sintering temperatures (1200ºC-1250ºC) in producing dense sintered akermanite ceramics.

1.4 Research Scopes

Generally, this work can be divided into two main parts: (1) The possibility of ultrasonic technology at different frequencies and temperatures in producing pure calcium and (2) to find out optimise sintering temperature (1200ºC-1250ºC) in producing dense sintered akermanite ceramics. The flow for this works is shown in Figure 1.1.

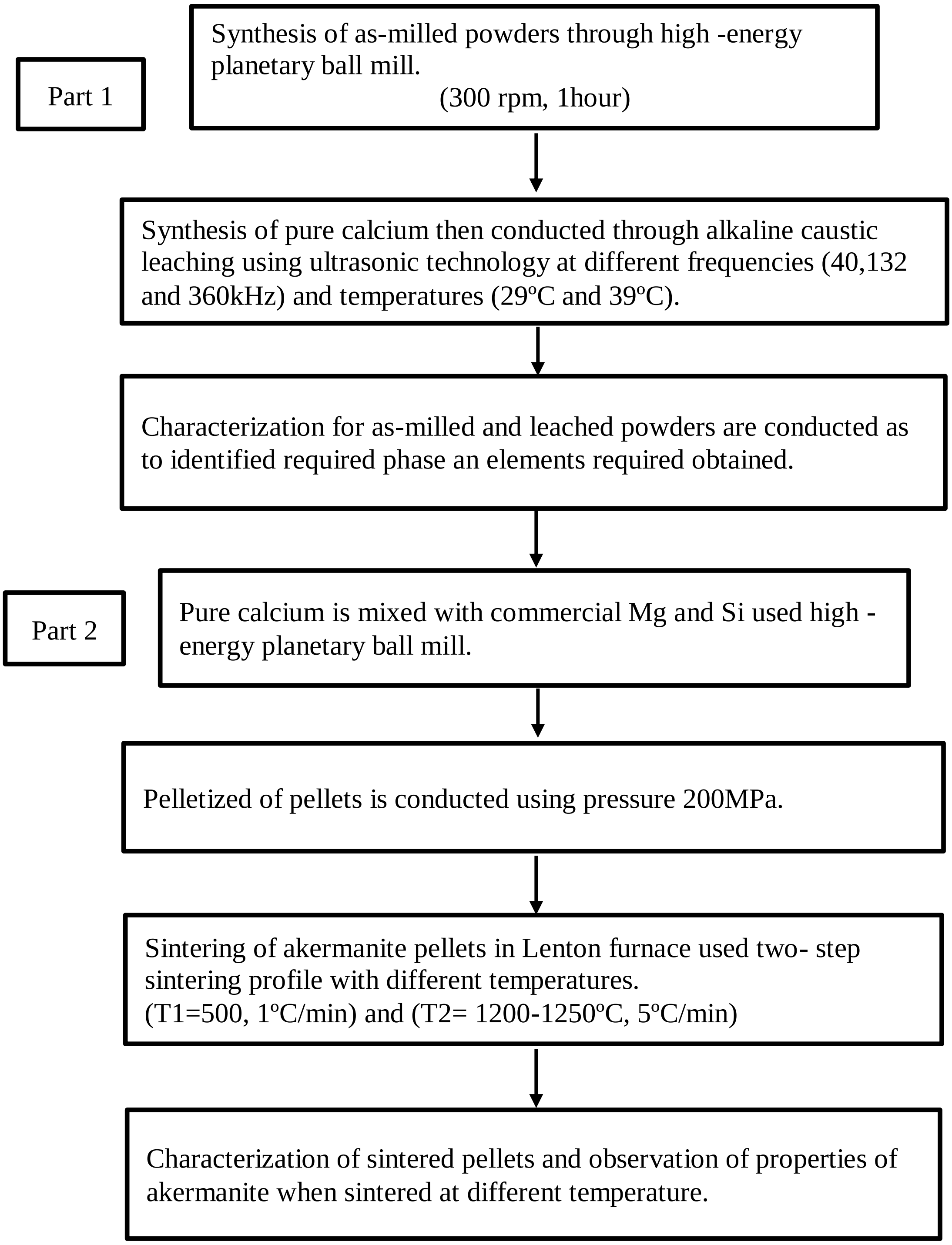

Figure 1. 1 Work flow for synthesis akermanite ceramics

CHAPTER 2

LITERATURE REVIEW

2.1 Biomaterials

Biomaterials are materials that created to interact with biological systems in order to treat, augment, or replace biological functions. Both biomaterials and biological systems interact in both directions. The usage of biomaterials may result in positive and negative responses due to the interface of biomaterials with biological systems and the dynamic interaction between them (Ng. *et al.*, 2019). Nowadays, biomaterials are highly used for various medical applications and the treatment of cardiovascular disease used biomaterials as well (Kalathottukaren *et al.,* 2018).

Besides, biomaterials can be divided into biological and synthetic biomedical, where synthetic biomedical is classified into ceramics polymers and metals. Biological materials consist of organic and inorganic compounds obtained from biological sources. In order to create biomaterials that will be used as body implants, the biomaterials must provide excellent mechanical stability, good inertness and biocompatibility and must be easy to fabricate. Many biomaterials applications are widely used, like cardiovascular implants, dental implants for tooth fixation, breast implants, heart valves, cochlear replacement, and drug delivery systems (Dharadar *et al.,* 2019).

2.2 Biomaterials for Bone Tissue Replacement

Bone tissue is recognized as a mineralised and viscous-elastic connective tissue that performs critical functions in our bodies like tissue support and protection, as well as mineral storage. Bone can adapt by remodelling itself and is controlled by its cells and various local and systemic factors. It is a complex process that involves both cellular reactions and the effects able to observe on the internal structure of the bone (Bilgiç *et* *al.,* 2020). Besides, as bone is living tissue, it involves resorption and deposition processes related to the release and use of calcium and phosphate. Somehow, the main bone cells that control this process are osteogenic cells, osteoclasts, osteoblasts, osteocytes, and bone-lining cells.

The osteoblast is important in bone tissue replacement as it aid in the formation of new bone by secreting osteoid, an organic bone matrix. They are most commonly found beneath the periosteum and close to the medullary cavity, with higher metabolic bone rates. Whereas Osteoclasts are multinucleated, large cells that resorb bone tissue by releasing lysosomal enzymes and acids. Osteocytes make up 90% of all cells in mature bone and are derived from trapped osteoblasts in newly formed bone tissue. They support cellular communication and the skeleton's daily functions by transporting nutrients and wastes. Finally, osteoblasts have covered the bones' surfaces, producing bone-lining cells. Their role is to release calcium when necessary, initiate bone resorption and remodelling, and potentially maintain bone fluid balance (Nikita,2017).

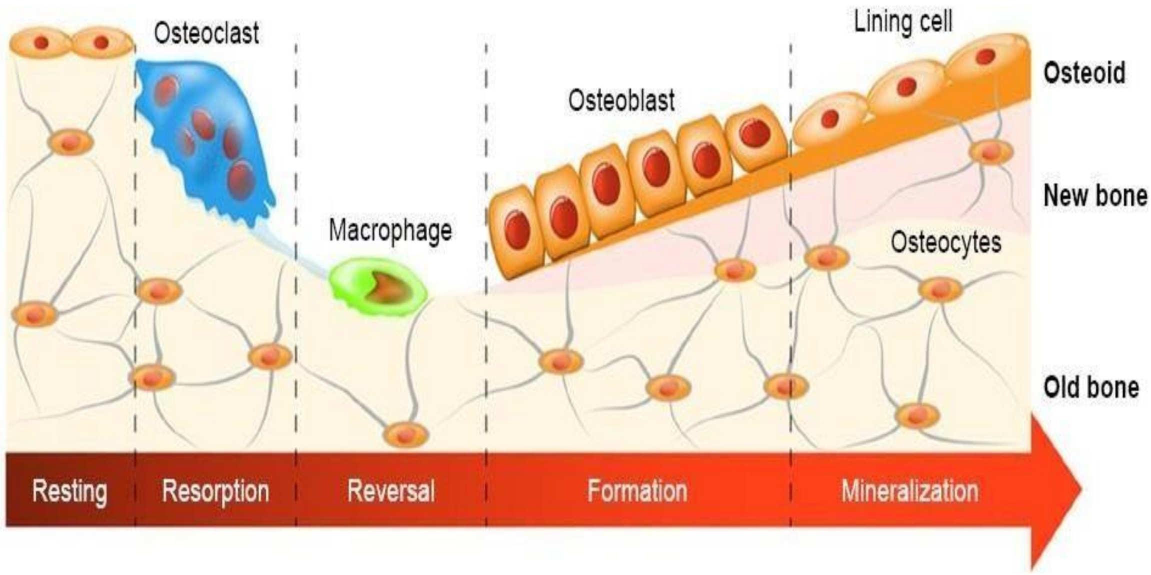

Figure 2. 1 The remodelling process of bone (Liwoska et al., 2018)

In bone structure there are several diseases that related to its which may cause by genetic, environments, infections and so on. Common diseases that affect the structure and function of bones are osteoporosis, osteopenia, osteogenesis imperfect, osteonecrosis, osteoarthritis, osteomyelitis and osteomalacia (Santhakumar,2022). The detail explanation about the types of bone disease are stated in Table 2.1:

Table 2. 1 Lists of bone disease (Santhakumar,2022)

Type of Disease	**Bone Condition**
Osteoporosis	Reduction in bone mass and mineral density. The bone's quality and structure may also change. Osteoporosis can weaken bones and increase the risk of fracture.
Osteopenia	A decrease in bone mineral density that is lower than normal but not low enough to be classified as osteoporosis.
Osteogenesis Imperfecta	A condition that causes bones to fracture or known as brittle bone disease. The condition is caused by a change or mutation in the genes that carry information for the production of a protein called type I collagen.
Osteonecrosis	It occurs when a bone's blood flow is disrupted, resulting in bone tissue death. This can result in bone breakdown and joint collapse.

Osteoarthritis	It can degrades cartilage, the tissue that covers the surface of joints, affecting the body's joint. Osteoarthritis can also cause bone shape changes.
Osteomyelitis	The bone is experienced infection and inflammation.
Osteomalacia	After formation, bone does not harden as it should. This metabolic bone disease occurs when the bone's mineralisation is incomplete.

2.3 Bioceramics

Bioceramics is a material used to repair or replace damaged bone tissues. Bioceramics can directly interact with the surrounding tissue, either supporting tissue growth or inducing new tissue regeneration for bioactive ceramics, depending on the application. It can also remain inactive at the application site, acting as a mechanical load carrier as bioinert ceramics (Roy *et al.*, 2017). Additionally, bioceramic materials can potentially replace damaged tissues while restoring the function of the existing tissue. ZrO_2, Al_2O_3 based materials, and composites are currently used in the fabrication of implants. Because of their mineral composition similarity to hard tissue, bioceramics such as hydroxyapatite, bioglass, and calcium phosphate are used as scaffolds, bone fillers, and coating agents. Bioceramics produce a greater tissue response than polymers and metals alone (Kumar et *al.*, 2018). Furthermore, bioceramics can be classified into calcium phosphate and calcium silicate, broadly used in medical and dentistry applications. Calcium phosphate and calcium silicate can be described as followed:

(i) Calcium Phosphate

Calcium phosphate (CaP) is the common name for a group of minerals that contain calcium cations (Ca^{2+}), orthophosphate (PO_4^{3-}), metaphosphate (PO_3), or pyrophosphate ($P_2O_7^{4-}$) anions, and occasionally hydrogen (H^+) or hydroxide (OH^-) ions. Besides, it is the primary inorganic constituent of bone about 60 wt.% and the primary constituent of tooth enamel which is Ca about 90% (Eliaz & Metoki, 2017).

(ii) Calcium Silicate

Calcium and silica ions have piqued the interest of biomedical researchers. The two ions are directly involved in many biological processes as example, calcium (Ca) is important in regulating cellular responses to bioceramics, promoting cell growth, and osteoblast differentiation. Meanwhile, silica (Si) plays an important role in bone calcification and is beneficial for bone density improvement and osteoporosis prevention. Calcium silicate ceramics include a wide range of trace metal containing calcium silicate-based compounds. It widely used in biomedical applications such as hard tissue texture repair, bone scaffolds, bone cements, and implant coatings (Srinath *et al.*, 2020).

Into the bargain, according to Ming Wan et al. (2019) bioceramics are biocompatible ceramic or glassy materials used to repair or reconstruct damaged human body parts. Bioceramics can be manufactured in a variety of forms (for example, powder, coating, and bulk) to perform various functions in human tissue repair or replacement. Ceramics, glasses, glass-ceramics, and composites are among them. Besides, bioceramics able to classify into three groups such in Figure 2.2.

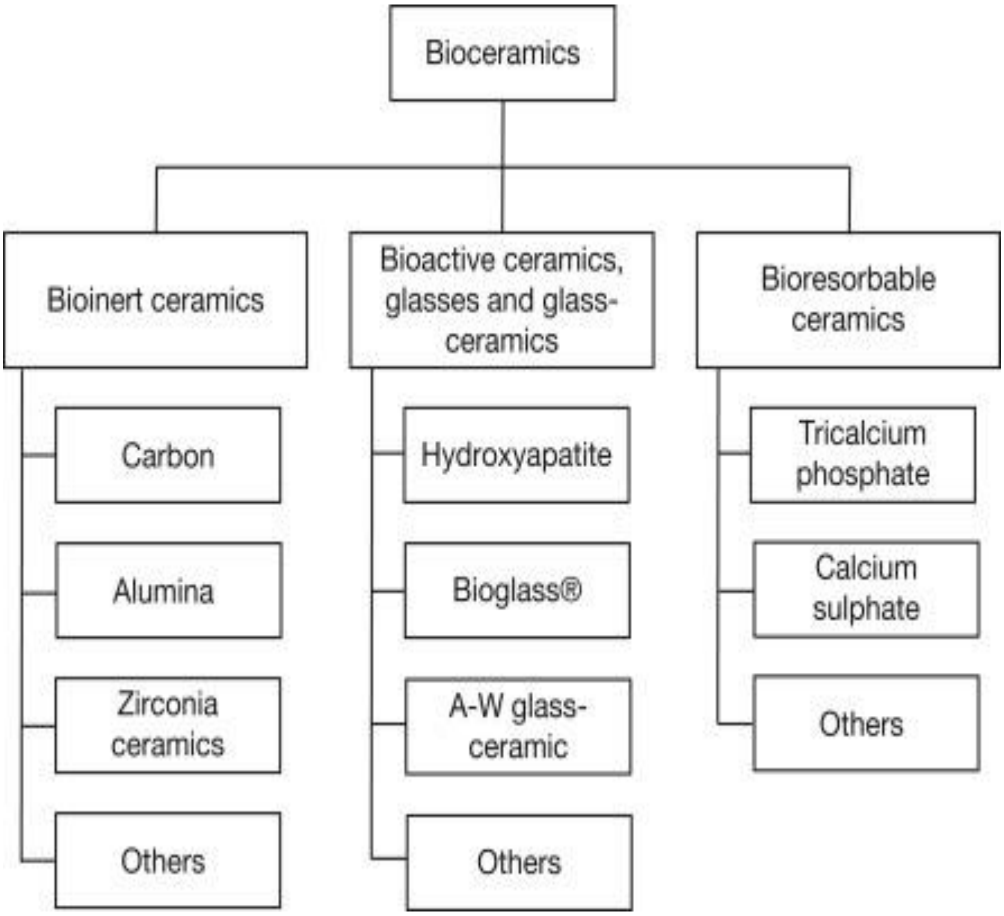

Figure 2. 2 Classification of bioceramics (Ming Wan et al., 2019)

In addition, bioceramics are biodegradable and are replaced by bone through a resorption or reconstruction process similar to that of natural bone. First, the ceramic grain boundaries are resorbed. This degradation of the material allows for the release of micro- or even nanoparticles, which cause biological reactions that can be useful in certain applications (P. Frayssinet *et al.*, 2011). In example this reaction can be observed through releasing of transient induction by calcium phosphate ceramics that caused foreign body reaction.

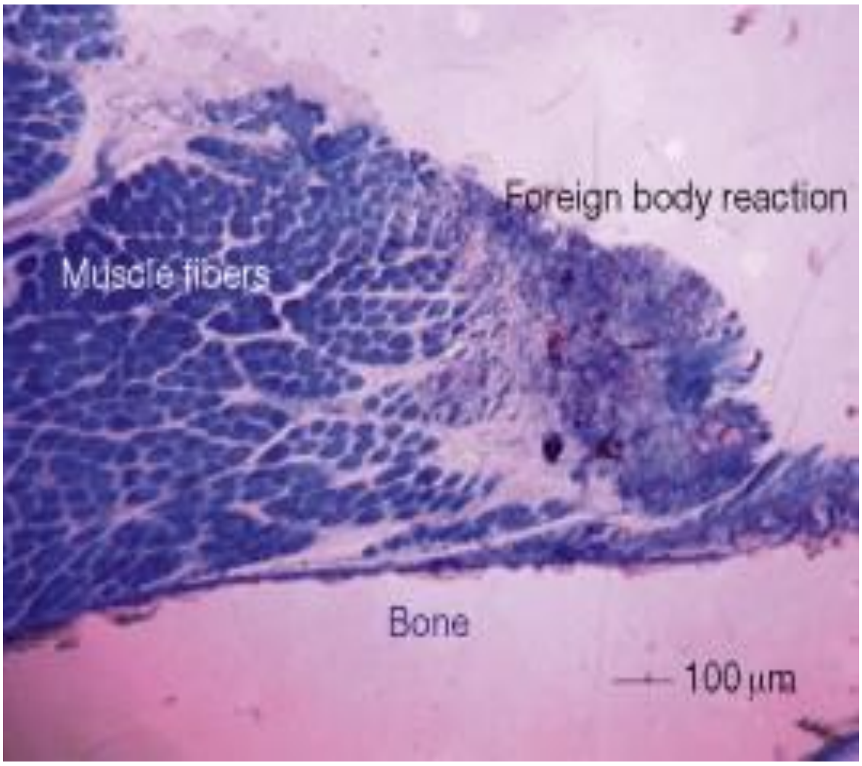

Figure 2. 3 Foreign body reaction due to transient induction (P. Frayssinet et al., 2011)

2.3.1 Bioceramics Scaffold

Three-dimensional tissue growth requires porous templates known as "scaffolds". Bioceramics, a subset of fully, partially, or non-crystalline ceramics (e.g., calcium phosphates, bioactive glasses, and glass-ceramics) designed to repair and reconstruct diseased body parts, have great promise as scaffold materials. A scaffold is a synthetic framework that guides two- or three-dimensional (2D or 3D) structures for both hard and soft tissue development in vitro and in vivo (Baino Francesco *et al.*, 2015).

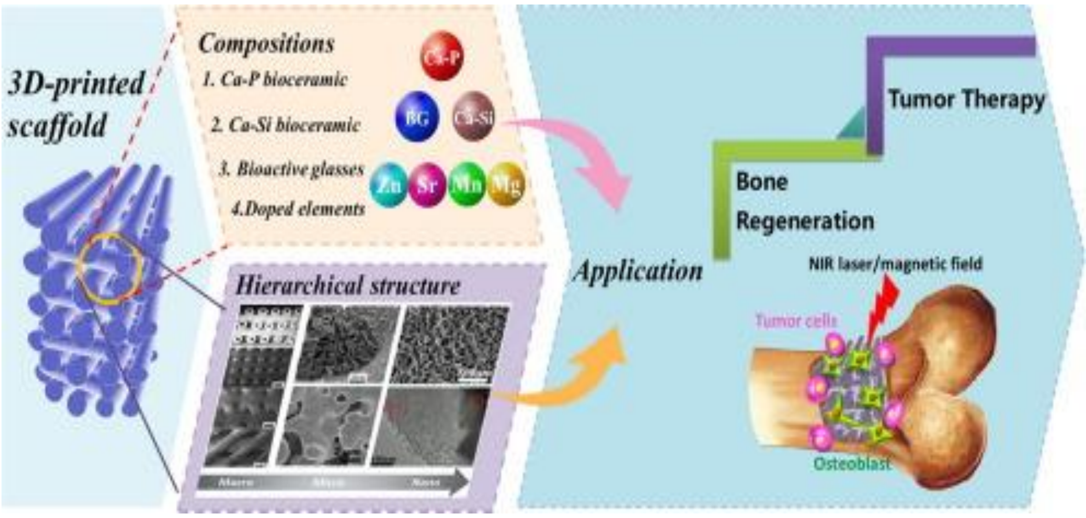

Figure 2. 4 Application of 3D printer scaffold for tumor therapy (Hongshi Ma et al., 2018)

Based on Hongshi Ma et al. studied, due to variation advantages like fast, precise and controllable fabrication, three-dimensional (3D) printing technology has been widely used in bone tissue engineering.

Scaffolds are important in tissue engineering because they can mimic the native extracellular matrix, and their properties have been shown to influence cell behaviour such as cell attachment, proliferation, and differentiation. Recent studies were focused on various aspects of scaffolds, such as the materials used in scaffold fabrication, surface modification of scaffolds, topography, and mechanical properties of scaffolds in relation to stem cell differentiation. Scaffolds are important in tissue engineering because they can mimic the native extracellular matrix, and their properties have been shown to influence cell behaviour such as cell attachment, proliferation, and differentiation (Ghasemi Mobarakeh *et al.*, 2015).

Based on Boehler et al. (2011) studied the immune response is a major concern in synthetic biomaterials used for scaffold fabrication, and it can be reduced by using materials that are inherently inert or by modifying scaffolds to avoid immune system detection. When compared to hydrophilic materials, hydrophobic materials tend to increase monocyte adhesion, resulting in a local immune reaction at the scaffold site.

2.4 Dental Waste

In the fabrication of dental moulds, gypsum is a vital material usually used due to its dimensions and stability properties and is reasonable and inexpensive. Nevertheless, it is still harmful to the environment as it can produce flammable and toxic gas, hydrogen sulfide, and will create the worst condition in the long term. According to Qiyoung Xu et al. (2011), the disposal of gypsum in landfills produces a lot of problems, such as workers' health safety and odours and causes damage to gas-to-energy systems. According to gypsum, this situation releases hydrogen sulfide gas (H_2S), where the concentration of this harmful gas is dangerous to the environment. Besides, based on Christopher Altamirano (2020) studied when the gypsum is not in use anymore and disposed of near the construction metabolic cycle will occur. The bacteria use calcium sulfate available in gypsum as a metabolic cycle and release hydrogen sulfide as by-products. Moreover, it produces inconvenient odours like rotten eggs and colourless gas, which are detected even at a low level.

In addition, Parimal Chandra Bhomick et al. (2014) stated that hydroxide sulfide gas (H_2S) is considered toxic as its threshold value is 10 ppm. It is easily recognised even at a low level due to its smell, similar to rotten eggs. Therefore, if the waste disposal is done unethically, it may create horrible environmental conditions in the future as the concentration of harmful gas produces too high.

Next, gypsum waste is already recognised as rich in calcium content. However, chromium (Cr^{3+}) needs to be eradicated in recycling the waste to get pure calcium. This is because chromium (Cr^{3+}) is also recognised as toxic material affecting humans and plants. This matter has already been discussed by Arun K. Shanker et al. (2005) where it affects plant growth as well as the quality of plants. It also can interrupt and damage the plant's psychological processes. Kirti Shekawat et al. (2015) also studied the effect of Cr^{3+} on human bodies. The routes usually exposed to chromium are ingestion, dermal contact, and inhalation. Chromium can affect human health where the condition can be classified into two types carcinogenic and non-carcinogenic, according to exposure period.

Gypsum is one of the mineral resources known as calcium sulfate with the chemical formula calcium sulfate dihydrate ($CaSO_4.2H_2O$). Nevertheless, gypsum is insoluble in water with similar characteristics to II-type calcium sulfate anhydrous. Therefore, as calcium sulfate dihydrate ($CaSO_4.2H_2O$) undergo a heating process, they change into β or α calcium sulfate hemihydrate. Meanwhile, the setting and hardening reaction, specifically called dissolution- precipitation reaction, can cause the transformation of phase from calcium sulfate hemihydrate into calcium sulfate dihydrate (Ishikawa, 2011). Instead of having poor solubility in water, gypsum is recognised as the most abundant secondary mineral in sulfide-rich tailing. This is due to sulfate content with a high concentration in gypsum that forms by oxidation of sulfide and a high concentration of calcium (Ca) (Blowes, 2014).

Calcium sulfate or gypsum is one of the inorganic salt where the solubility of gypsum in water is affected by temperature. Therefore, according to Leiteng Shen et al. (2019), various temperature ranges usually affect gypsum's behaviour or chemical properties. The gypsum can present in a stable structure when the temperature is between 273.15K to 315.95K, where the sturdy phase of anhydrite emerges above 315.95K. Meanwhile, hemihydrate forms a metastable phase in all ranges of temperature. Calcium sulfate forms stable hydrates in an aqueous solution with several chemicals: anhydrate, hemihydrate and dihydrate. On top of that, the condition of $CaSO_4$ hydrate is influenced by temperature as well, other than the condition of the solution. The effect of temperature on solubility and different formation of phases can be identified in Figure 2.5 (Shen *et al.*, 2019).

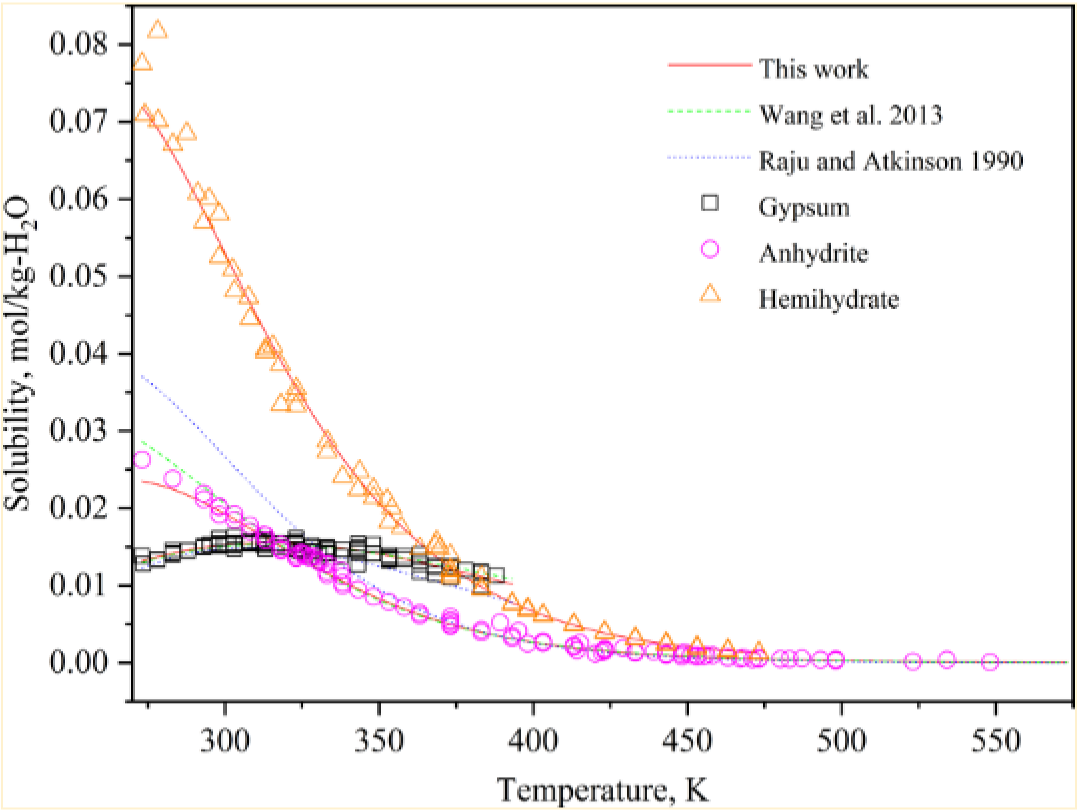

Figure 2. 5 The graph of phases formation with various temperature and solubility (Shen et al., 2019)

The crystalline structure of calcium sulfate dihydrate appeared as a slaty structure consisting of two layers structure with anion groups [SO_4^{2-}] between the layers. Then there is cation Ca^{2+} associated with the anion groups, and there are H_2O molecules too in the structure. This kind of structure imparts perfect cleavage of calcium sulfate dihydrate. In addition, based on electron micrograph pictures, calcium sulfate dihydrate has a long and sharp prismatic shape with lengths below 15µm and frequently growth in parallel form. The image in Figure 2.6 shows the crystalline particles of calcium sulfate dihydrate (Plugin *et al.*, 2014).

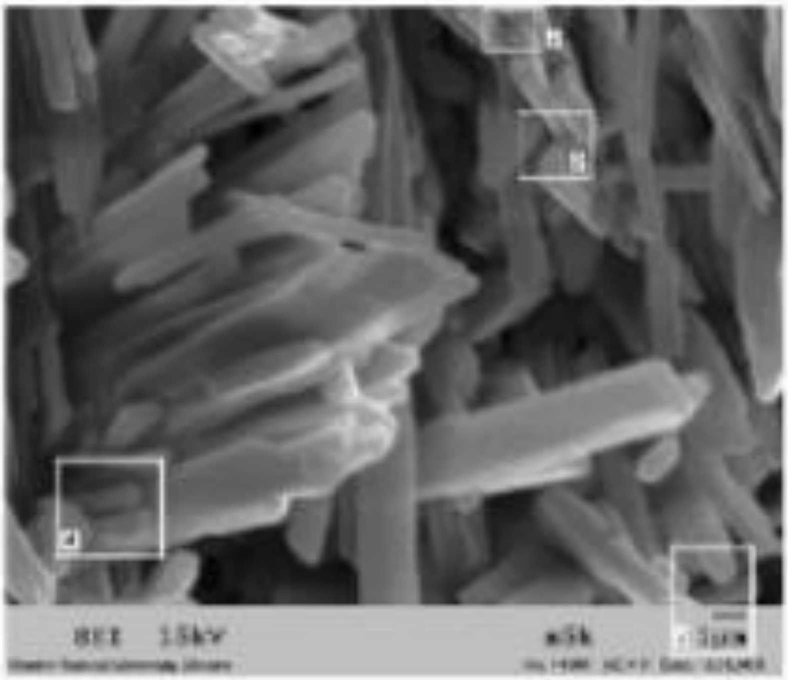

Figure 2. 6 Image of calcium sulfate dihydrate from an electron micrograph (Plugin et al., 2014)

2.4.1 Recycling of Dental Mould Waste

According to Nevrlý V. et al. (2021) waste can be reused, recycled, and directed toward the production of value-added goods to promote long-term growth. This protects the environment while also establishing a zero-waste standard for obtaining value-added goods. Waste management is now a top priority for achieving sustainable development.

Dental waste like gypsum can be recycled and reused to reduce the disposal amount in landfills and, at the same time, save the environment in the long term. Throughout the research done by Dr. Ravikiran et al. (2020), gypsum and plaster used to fabricate dental mould can be treated with an ammonium bicarbonate solution of 20% concentration. The ammonium bicarbonate solution with a 20% concentration is capable to kills 99.9% of microbes in the waste in 3 hours. Into the bargain, ammonium bicarbonate solution disintegrates the waste into non-toxic chemicals like calcium carbonate and calcium sulfate in the form of sludge.

Moreover, ammonium bicarbonate solution has characteristics of antifungal and antibacterial. Besides, calcium carbonate is widely used in Malaysia's metallurgy industry, whereas ammonium sulfate is used in the pharmaceutical industry, textile, fertilisers and fire extinguisher powders.

2.5 Akermanite

Akermanite ($Ca_2MgSi_2O_7$) ceramics, known as calcium silicate-based ceramics, have recently received a lot of attention because of their outstanding *in vitro* bioactivity, biocompatibility, biodegradability, and good mechanical properties. Dasan Arish et al. (2019), stated that The PDCs route is one of the alternative ways in produced akermanite foams). It demonstrates excellent bioactivity and biocompatibility.

The most common methods for producing akermanite are sol-gel-based methods. However, the raw materials for these processes are expensive, and the products would have a high carbon content, inhibiting densification during sintering. Furthermore, the process must be closely monitored because several steps are involved. Moreover, using these methods for preparing akermanite is extremely time-consuming (Sharafabadi *et al.*, 2016).

Tetraethyl orthosilicate (TEOS) has traditionally been used as the primary network forming agent in sol-gel methods. The primary reason for using TEOS is that simple changes in synthesis conditions such as pH, temperature, and additives allow for the formation of robust networks with moderate reactivity and a high degree of control (P.Yang *et al.*, 2012). The transition of colloidal solution to an interconnected gel network is defined as a sol-gel process (gelation). The additional processing stages after gelation are non-redundant and may be combined depending on the application's specific needs. Figure 2.7 illustrates the process involved in sol-gel methods.

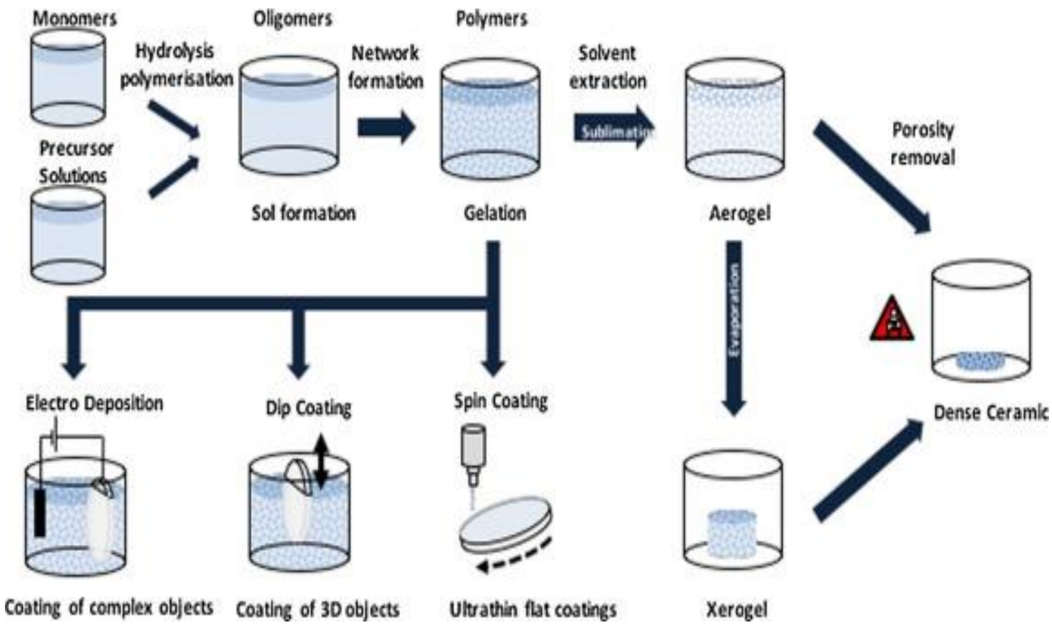

Figure 2. 7 The synthesis route of sol-gel method (P.Yang *et al.*, 2012)

The processes depicted in Figure 2.7 are by no means exhaustive. Depending on the application, these stages can be extended, changed, or removed entirely, except for solvation and gelation. However, the steps that allow for hydrolysis and condensation reactions remain constant in producing sol-gel derived bioactive materials (Gareth J. *et al.*, 2016).

Other than that, traditional scaffold fabrication methods, such as gas foaming, fibre bonding, and phase separation, are incapable of accurately controlling pore morphology, pore size, and overall porosity. Therefore, the selective laser sintering (SLS) technique, a CAD-based rapid prototyping method with excellent spatial control over architecture, was developed to improve pore structure control (Z. Han *et al.*, 2014).

2.6 Mechanical Process

As the dental mould collected is large, the mould needs to undergo a size reduction process. The size reduction is crucial to increase the efficiency of the chemical reaction during powder synthesis. The relation of particle size with chemical reaction has been discussed by Yonqiang Xue et al. (2011), where particle size affected the kinetic parameters. When the diameter of the size of particles decreases, the reaction rate increases.

Thus, the dental mould needs to go through the milling process instead of crushing the dental mould using a cone crusher. Crushing using a cone crusher is insufficient, and the milling stage will help obtain the more acceptable size of powders for synthesis.

2.6.1 Dental Mould Crush

As dental mould is hard, thus to make crushing process easier cone crusher is used for crushing the mould. The Cone crusher has a similar mechanism to the gyratory crusher where the process already discussed by Oleg D. Neikov (2019) in the Handbook of Non-ferrous metal powders. During the materials crushing process, crushing surfaces will approach each other, and crushed materials will fall through the opening before reaching the tray.

Furthermore, cone crushers have a similar design with gyratory crushers. Yet, the spindle is located at the bottom of the gyrating cone for cone crushers, which contrasts with the gyratory crusher. Ashok Gupta et al. (2016) also studied the cone crusher design with a larger head-to-depth ratio than a standard gyratory crusher. Cone angles are flatters to keep the particles between the particles' crusher surface longer to produce the finer size of powders. Besides, the concave parts and metal slopes are parallel to each other.

Strong springs or hydraulics are used to hold the concave to avoid damage on the crushing surface. Figure 2.8 illustrates the schematic diagram of the cone crusher.

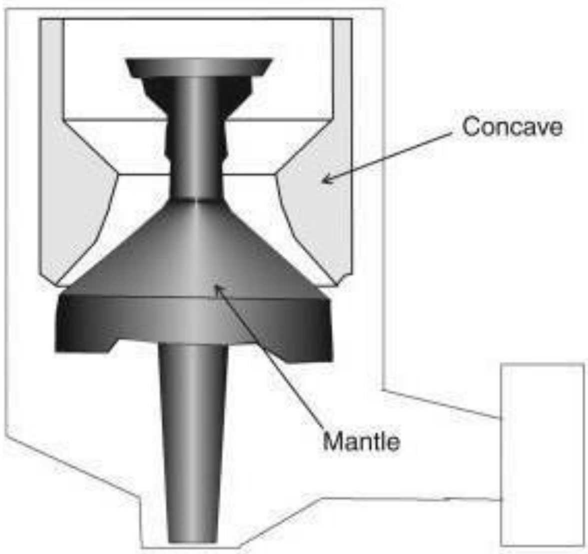

Figure 2. 8 Schematic diagram of cone crusher (Gupta et al., 2016)

2.7 High Energy Ball Milling

The milling process is vital to produce the required size of particles before proceeding to the synthesis stage. Ajay Vsudeo Rane et al. (2018) stated that the high energy ball milling process involved high energy collision of the ball during the ball milling process. Instead of being called ball milling, it is also known as mechanical alloying. Other than producing fine powders and uniform dispersion of oxide particles in nickel-based super alloy that is unable to produce by conventional powder metallurgy methods. High energy ball milling can also modify certain situations, such as changing the reactivity of as milled products or inducing a chemical reaction.

Meanwhile, Ghader Faraji et al. (2018) discussed the mechanism of high energy ball mill During the ball milling process, milling bowls and ball have contrasting rotation directions that cause the consequence of alternate synchronising of centrifugal force. Hence, it creates friction due to hard milling balls and a mixture of powders that alternately ground on the bowl's inner wall and strike the wall opposite. On top of that, as there is gravitational acceleration, the normal direction consists of the impact energy of milling balls recorded as up to 40 times or higher. The motion of the balls and powders mixture is shown in Figure 2.9.

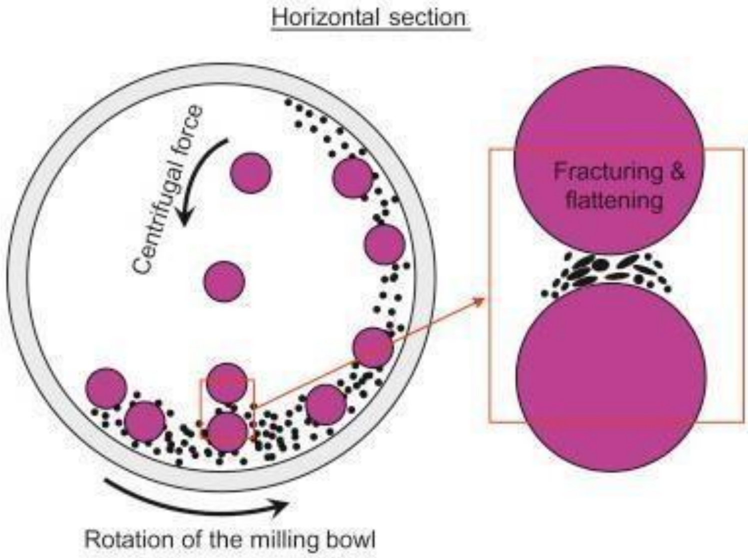

Figure 2. 9 Motion of balls and powders mixture (Faraji et al., 2018)

The ball milling can be classified into four stages which are the initial stage, intermediate stage, final stage and completion stage. In the initial stage, powders are flattened by compressive force due to ball impact. As a result, the particles will undergo deformation or change shape due to microforging, but it does not affect the mass net change. Next, in the intermediate stage, a significant change still occurs compared to the initial stage. After that, the powders become more refined in the final stage, and there is a reduction in the particle size of the powders. Finally, the completion stage is where the powders appear in extreme deformation and exhibit a metastable phase.

2.7.1 Grinding and Milling

Ball mills are widely used either in wet or dry milling, where usually used for batch and continuous operation and production of small or large scale. Based on Oleg D. Neikov (2019) studies, the energy of grinding is transferred into the milling media like balls, rods, and pebbles when the mill body is moved. Additionally, the ball medium mill can be divided into tumbling ball mills, vibration mills and planetary mills based on the mill body motion. Supposedly the usage of the ball mill must be at full-scale capacity during the grinding process.

The ball mill body has various forms like cylindrical, conical and tubular. The discharging method of milling can be classified into mills with a free discharge of ground product through hollow trunnion, mills with external separation in which the products are separated from under milled powders outside of the mill drum in the separator and mills with the discharge along with the drum through the cylindrical sieve.

2.7.2 Planetary Ball Mill

A planetary ball mill contains rotating mill pots and a revolving base disk. The planetary ball mill materials are ground by centrifugal force produced through rotation and revolution. There are various grinding pots and balls materials such as silicon nitride, agate, zirconia, sintered corundum, chrome nickel steel, chrome steel, plastic polyamide, and tungsten carbide. Last but not least, Fritsch Pulverisette P-5 four station planetary ball mill is commercially used nowadays like shown in Figure 2.10 (Neikov, 2019).

Figure 2. 10 Fritsch Pulverisette P-5 four station planetary ball mill (Neikov, 2019)

2.8 Ultrasonic Cleaning

In order to remove chromium content in gypsum, the leaching process is conducted using ultrasonic cleaning. Ultrasonic cleaning involves high frequency and high intensity of sound waves as to raise the efficiency of impurities removal. As F.J Fusch (2015) stated, nowadays the ultrasonic waves can be customised to gain optimum range effects and are widely used for various applications. Hence, ultrasonic is an option for leaching of gypsum as the high frequency may help change the chemical bonding and remove the chromium content optimum. In addition, ultrasonic technology is known as unique due to its ability to remove impurities or contaminants that other technology cannot conduct. Besides, it can also help to conduct the cleaning process effectively in areas that cannot be accessed by other technology.

Other than that, the power used on specific frequency towards the reaction within the solution or cleaning process. For example, S.B. Awad et al. (2020) studied the effect of powers and found out that the lower the powers used, the lower the particle removal rate. Moreover, the rate of erosion or erodibility on the material surface also decreases when the power set for the cleaning is low. Besides, based on the study 80% usage of