Design of Laboratory Scale Prototype of Hydrothermal Crystallizer

By

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by.

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Main Supervisor

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Tronoh, Perak

January 2008

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD NAZRI BIN ME

ABSTRACT

For this project, have been decided that the crystal growth cell will totally be made from glass and will have a separated disc at the middle to separate two compartments. The separated area is to create the convection movement inside the cell and to help in producing the crystal. In this report, I will discuss more about the convection movement. I have also included some useful information about the benefit of the crystals in several fields. This project can be commercialized and the income is quite good. The crystallization cell is a glass cylinder, fitted with two water jackets each connected to a thermostat and a submersible pump. The diameter of the cylinder is about 10 cm. And the height of the cylinder is about 20 cm. The cylinder has two compartments separated by a separating disc. The separating disc has 2% holes on it, which the hole area is 1mm. It connected to the submersible pump, at the top compartment and to the thermostat bath at the bottom one.

ACKNOWLEDGEMENT

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I must also acknowledge the endless help and support received from my supervisor, AP. Dr. Bambang Ariwahjoedi throughout the whole period of completing the final year project. His guidance and advices are very much appreciated.

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CHAPTER 1

INTRODUCTION

Since this project start, the main focus is to study the structure of the crystal, to design a growth cell using glass as the main material, and to know the principles that being used in this project.

1.1 Background of study

Hydrothermal method includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibrium since the turn of the century. George W. Morey at the Carnegie Institution and later, Percy W. Bridgman at Harvard University did much of the work to lay the foundations necessary to containment of reactive media in the temperature and pressure range where most of the hydrothermal work is conducted.

Hydrothermal method can be defined as a method of synthesis of single crystals which depends on the solubility of minerals in hot water under high-pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth.

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition.

1.2 Problem statement

Various important crystals for very useful materials applications require to be grown in relatively large size. The available techniques to grow large crystals mostly are the expensive gas phase technique such as CVD or even through the molten chzochralsky technique which is also very expensive. One technique to grow a relatively large crystal which is relatively cheap is through solution technique, by the so called hydrothermal method. Due to its relatively simple and inexpensive nature, various variables governing this hydrothermal technique should be studied by building a laboratory scale crystallizer.

1.3 Objectives and scope of study

The main objective of this study is to design and build lab scale prototype of hydrothermal crystallizer which work to produce certain selected crystals. Other objectives are:

- To fulfill the university's requirement
- To study the behavior of the crystals
- To learn about the crystal growth.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Theory

In 1839, the German chemist Robert Whilhelm Bunsen contained aqueous solutions in thick-walled glass tubes at temperatures above 200°C and at pressures above 100 bars.[2] The crystals of barium carbonate and strontium carbonate that he grew under these conditions mark the first use of hydrothermal aqueous solvents as media. Other early reports of the hydrothermal growth of crystals were by Schafhäult in 1845 and by de Sénarmont in 1851 that produced only microscopic crystals [3]. Later G. Spezzia (1905) published reports on the growth of macroscopic crystals [4]. He used solutions of sodium silicate, natural crystals as seeds and supply, and a silver-lined vessel. By heating the supply end of his vessel to 320-350 °C, and the other end to 165-180 °C, he obtained about 15 mm of new growth over a 200 day period. Unlike modern practice, the hotter part of the vessel was at the top. Other notable contributions have been made by Nacken (1946), Hale (1948), Brown (1951), Walker (1950) and Kohman (1955)[5].

A large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: elements, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germanates etc. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals which have been efficiently grown are emeralds, rubies, quartz, alexandrite and others. The method has proved to be extremely efficient both in the search for new compounds with specific physical properties and in the systematic physicochemical investigation of intricate multicomponent systems at elevated temperatures and pressures.

2.2 The Growth Cell

The crystallization cell is a glass cylinder, fitted with two water jackets each connected to a thermostat and a submersible pump. The diameter of the cylinder is about 10 cm. And the height of the cylinder is about 20 cm. The cylinder has two compartments separated by a separating disc. The separating disc has 2% holes on it, which the hole size is 1mm. It connected to the submersible pump, at the top compartment and to the thermostat bath at the bottom one.

2.3 The Submersible Pump

A submersible pump is a pump which has a hermetically sealed motor close-coupled to the pump body. The whole assembly is submerged in the fluid to be pumped. The advantage of this type of pump is that it can provide a significant lifting force as it does not rely on external air pressure to lift the fluid.

A system of mechanical seals used to prevent the fluid being pumped from entering the motor and causing a short circuit. The pump can either be connected to a pipe, flexible hose or lowered down guide rails or wires so that the pump sits on a "ducks foot" coupling, thereby connecting it to the delivery pipe work.

Submersible pumps are found in many applications, single stage pumps are used for drainage, sewage pumping, general industrial pumping and slurry pumping. They are also popular with aquarium filters. Multiple stage submersible pumps are typically lowered down a borehole and used for water abstraction or in water wells.

2.4 Thermostat

A thermostat is a device for regulating the temperature of a system so that the system's temperature is maintained near a desired *set point* temperature. The thermostat does this by controlling the flow of heat energy into or out of the system. That is, the thermostat switches heating or cooling devices on or off as needed to maintain the correct temperature.

CHAPTER 3

METHODOLOGY

3.1 Project Work

Reference from book, journal and magazine has been useful guideline in gathering information regarding proposed topic. However it is difficult to obtained exact information. Literature review has been done by referring all sources available either by rental the books from IRCUTP (Information Resource Centre Universiti Teknologi Petronas) or surfing the internet. Most of the information were discussing in different sub topic and need to be correlated for each part and this need to be done as soon as possible. It also including revising all lab related lab work that need to be perform in the future finding.

After all necessary information has been collected, it comes to part of identifying and selecting type of method to be used. The method to be used is the temperature -difference method using the crystallization vessels, autoclaves. These are usually thick-walled steel cylinders with a hermetic seal which must withstand high temperatures and pressures for prolonged periods of time. Furthermore, the autoclave material must be inert with respect to the solvent. The closure is the most important element of the autoclave.

3.2 Hydrothermal Growth Method

A vertical growth cell is divided by a perforated disc into two zones, the walls of which can be kept at controlled temperatures. The upper zone contains the seeds to be grown, the lower zone contains the nutrient, i.e. a powdered crystalline mass to be dissolved and transported to the seeds. The initial solution is saturated at a temperature T_s, the lower zone is heated at $T > T_s$, while the upper zone is kept at T_s.

A convective movement sets in, bringing to the upper zone a solution concentrated by the dissolution of the nutrient. The fluid arriving in the upper zone is cooled, becomes correspondingly supersaturated and the seeds grow.

In this description it is accepted that the destabilizing temperature gradient is sufficient to induce convection in a fluid where a strong stabilizing concentration gradient exists. That stabilizing effect of an extremely low concentration gradient can be overcome only by an extremely high temperature gradient, in other words it is hard to see how convection can ever occur in such systems. The convective movements described in the literature are difficult to understand from a fluid mechanics point of view.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 The crystals

A *crystal* is a solid formed by the solidification of chemicals, has a regularly repeating internal arrangement of atoms and molecules, and is bounded by external plane faces. Crystal particles form a variety of geometrical shapes due to their internal compressions. Crystals have aesthetic properties that have long made them attractive in jewelry. But they also have some properties that make them very important to the electronics and optical industries. Today, crystals are used in just about every type of modern technology.

Crystals are familiar to everyone, common examples being salt and sugar. Less common but more alluring are diamonds and other gemstones. More prosaic are the innumerable crystals manufactured in the bulk, fine chemical and pharmaceutical industries, in both primary products, secondary formulations and their intermediates. As illustrated by the crystal products in Table 1.1, their range is immense and includes some highly sophisticated materials. Similarly, worldwide production rates and value are ever increasing.

Table 1.1 *Some industrially important particulate crystals*

Bulk chemicals	Catalysts	Ceramic precursors
Detergents	Dyestuffs	Electronic materials
Fertilizers	Fiber intermediates	Fine chemicals
Foodstuffs	Polymers	Pharmaceuticals

4.2 The convection movement

Convection in the most general terms refers to the movement of molecules within fluids (i.e. liquids, gases and rheids). There are many type of convections such as natural convection, forced convection, oceanic convection, buoyancy induced convection, mantle convection and others.

In this project, the principle of the forced convection is being used. Natural heat convection (also called free convection) is distinguished from various types of forced heat convection, which refer to heat advection by a fluid which is not due to the natural forces of buoyancy induced by heating. In forced heat convection, transfer of heat is due to movement in the fluid which results from many other forces, such as (for example) a fan or pump. A convection oven thus works by forced convection, as a fan which rapidly circulates hot air forces heat into food faster than would naturally happen due to simple heating without the fan. Aerodynamic heating is a form of forced convection. Common fluid heat-radiator systems, and also heating and cooling of parts of the body by blood circulation, are other familiar examples of forced convection.

4.3 The temperature-differences method

The most extensively used method in hydrothermal synthesis and crystal growing. The supersaturation is achieved by reducing the temperature in the crystal growth zone. The nutrient is placed in the lower part of the growth cell filled with a specific amount of solvent.

The cell is heated in order to create two temperature zones. The nutrient dissolves in the hotter zone and the saturated aqueous solution in the lower part is transported to the upper part by convective motion of the solution. The cooler and denser solution in the upper part of the autoclave descends while the counterflow of solution ascends. The solution becomes supersaturated in the upper part as the result of the reduction in temperature and crystallization sets in.

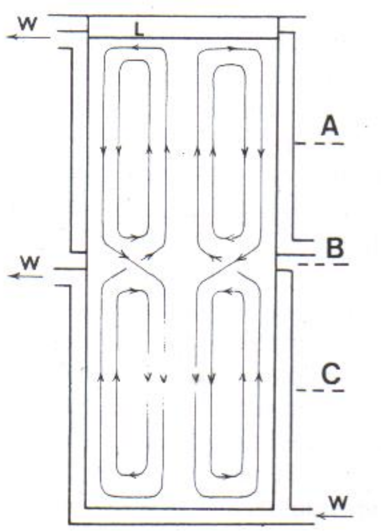
4.4 Crystal Growth without the Separating Disc

The temperature of the lower zone is about 37 to 40 ^oC and the upper zone is at the room temperature, the convection is symmetrical about the vertical axis. In the lower zone, the fluid sinks along the axis and rises along the walls, in the upper zone it rises along the axis and sinks along the walls. In the middle of the cell the flows intercross.

At A and C (figure) the temperature at a given point is constant. It is probable that the region of varying temperature corresponds to unique direction of flow (downwards in A, upwards in C). At B, where the flows intercross, the temperature at a given point is not constant, it varies randomly with amplitude of about 1 ^oC around the mean value. This indicates that here the fluid movement is not steady; no obvious periodicity could be detected. The temperature along the vertical axis is approximately constant in the whole cell.

Under these conditions, without a separating disc, it has always been impossible to obtain some crystal growth. The reason is that the convection affects only the fluid where there is no stabilizing concentration gradient.

Figure 4.1: Convective movement without the separating disk



4.5 Crystal Growth with the Separating Disc

The separating disc, thickness 1mm, open surface 2% about the total area, diameter of holes 1mm, being placed at the middle between two compartments. The convective movement may quite different from the previous one; there is no direct passage of fluid from one compartment to the other. In each zone there is an individual convection cell with symmetry, close to the disc the movement tangential. Under these conditions the temperatures of the two zones are quite different. The temperature of the disc is intermediate between those of the two zones and explains the convection in each zone. Only under these conditions is it possible to grow onto a seed.

The mass transfer between the two compartments probably occurs by the deflection at the holes of the tangential flow along the disc, this known as boundary-layer suction. Small quantities of more concentrated hot fluid pass from the lower to the upper zone, mix into a less concentrated cold solution and supersaturate it slightly.

There is an independent axisymmetrical convection in each compartment. The mass transfer between the two compartments probably occurs by the deflection of the boundary layers at the holes of the disc. The super saturation in the growth zone is much smaller than that given by the ratio of the saturation concentrations at the mean temperatures of the two zones.

Figure 4.2: Convective movement with the separating disk

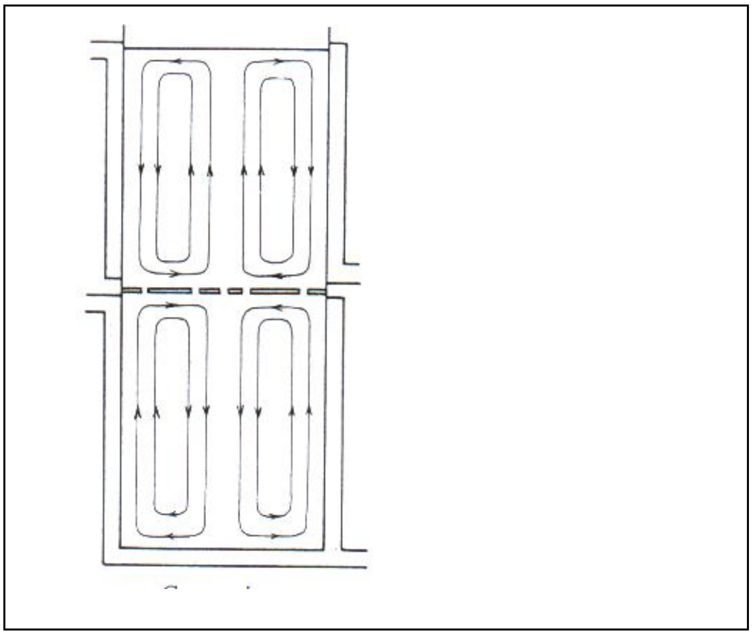


Figure 4.3: AutoCAD drawing

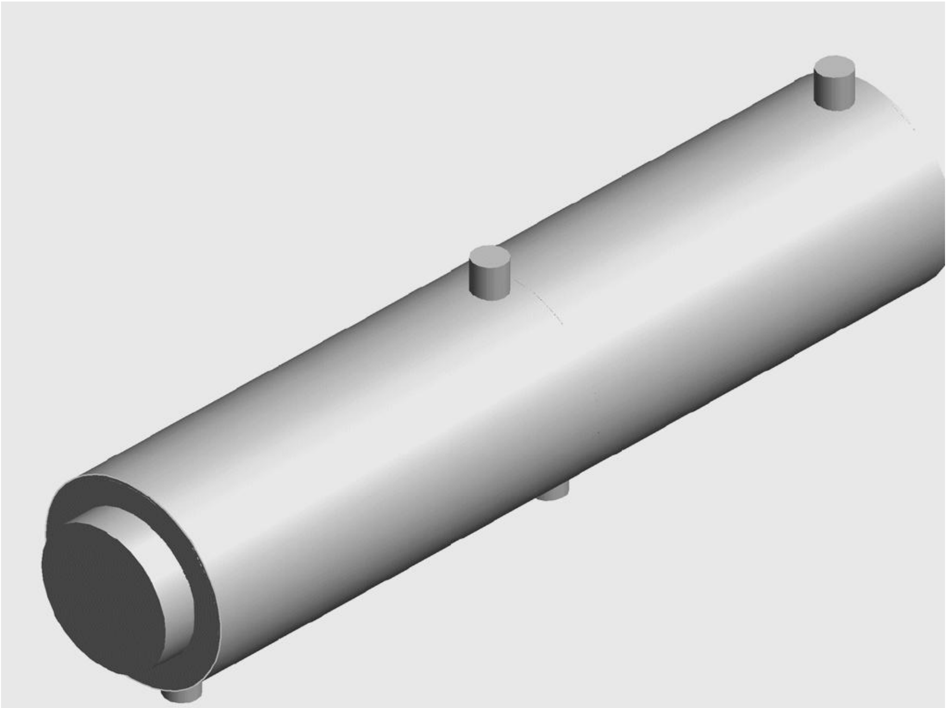


Figure 4.4: Isometric drawing

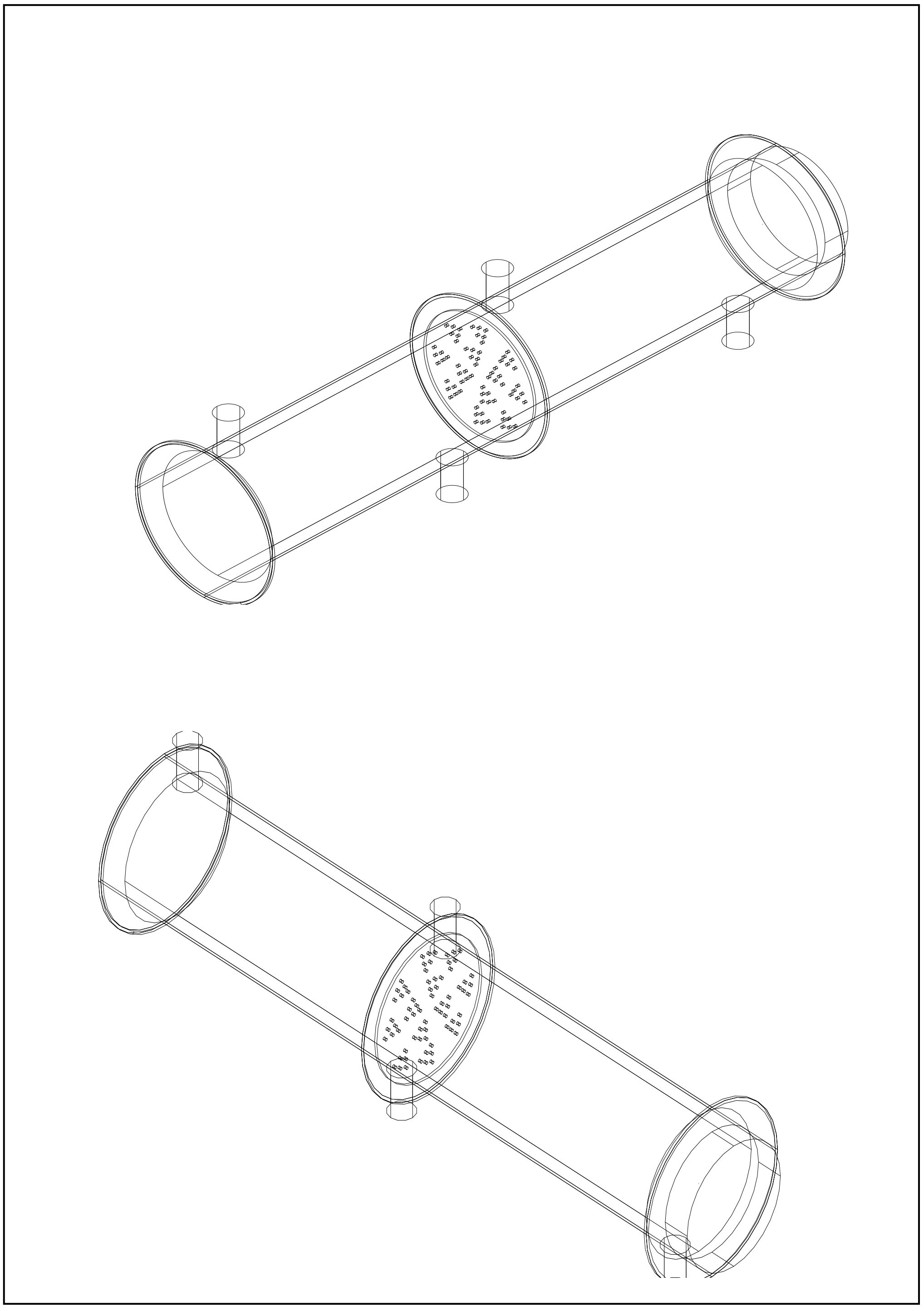


Figure 4.5: Top view

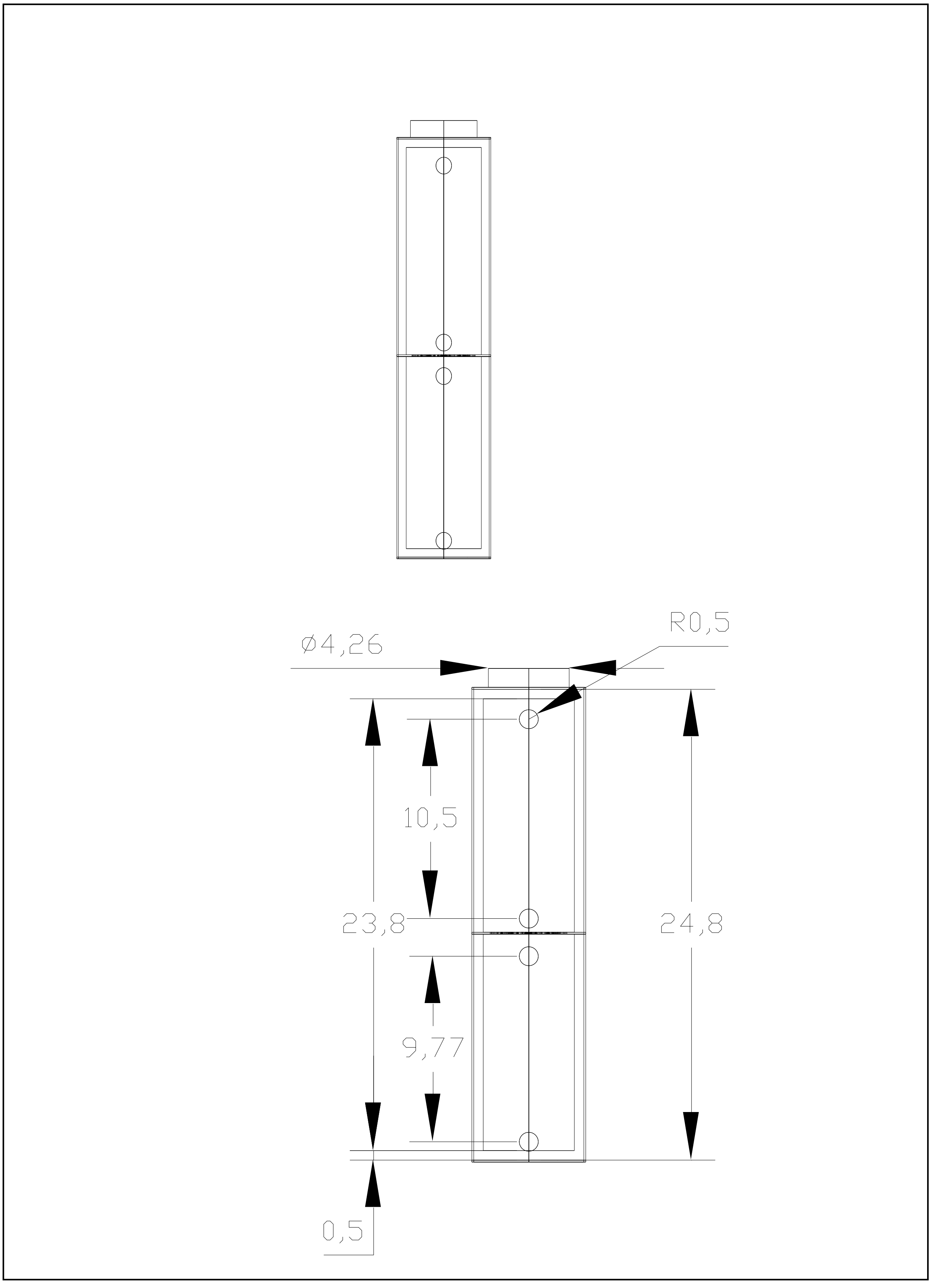


Figure 4.6: Side view

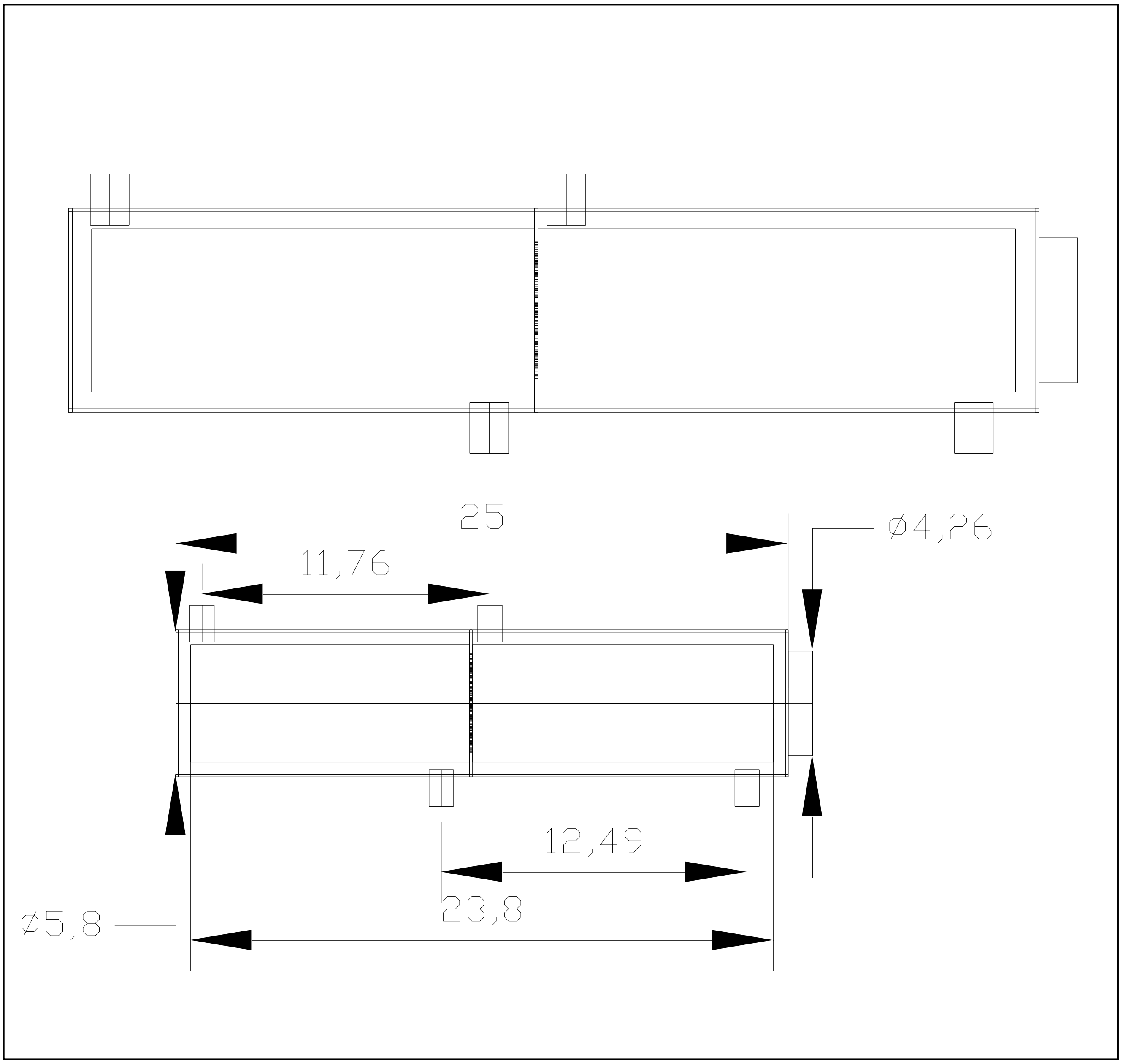
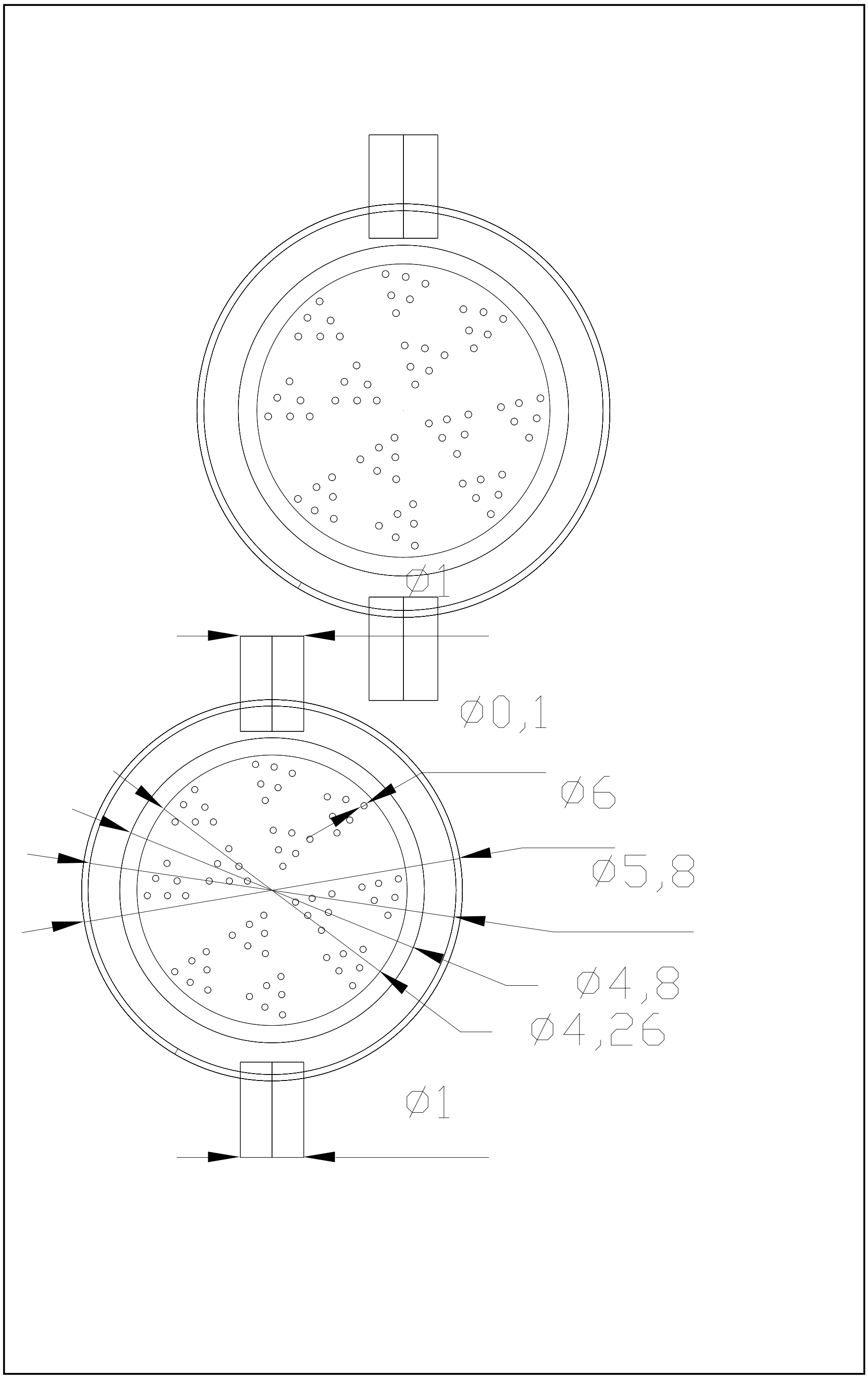


Figure 4.7: Front view



CHAPTER 5: CONCLUSION

5.1 Conclusion

As mentioned earlier in the objective, the main purpose is to design lab scale prototype of hydrothermal crystallizer which work to produce certain selected crystals. Here, it is importance to identify all necessary parameter. Those parameters can be useful in designing the laboratory scale prototype.

Design principle of the hydrothermal crystallizer is first studied and understood, afterward a technical drawing for the reactor should be completed and subsequently submitted to the glass blower for commission. On the completion of the commissioned reactor, it is ready for testing using the most favourable chemical crystals obtained from earlier selection.

5.2 REFERENCES

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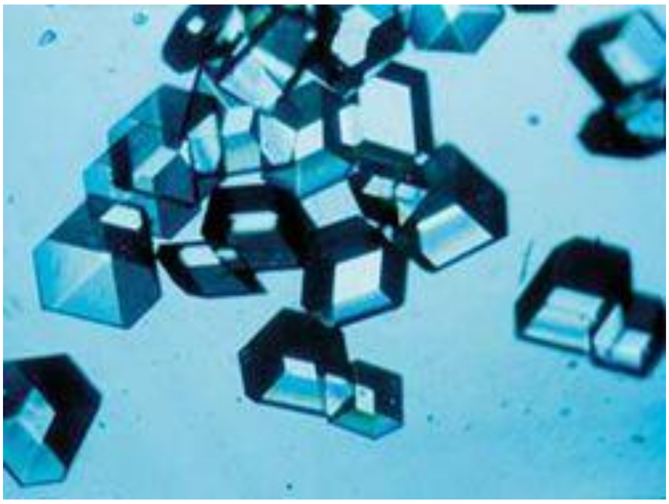
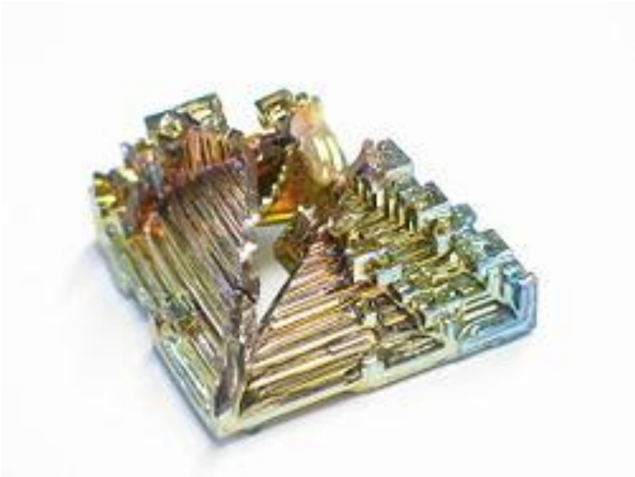
APPENDICES

Ice crystals



Insulin crystals



Bismuth crystals

Quartz crystal

Jewellery made from crystal

Jewellery made from crystal

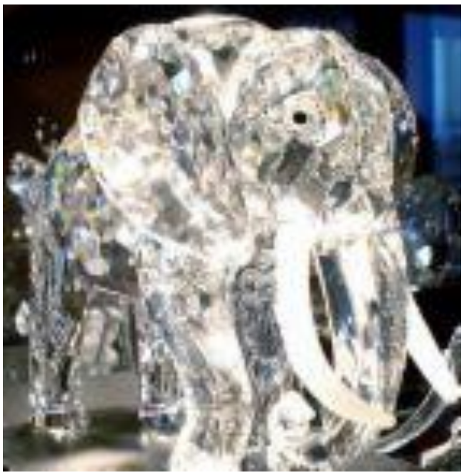
Decorative item made from crystal

Raw crystal


Jewellery made from crystal


Jewellery made from crystal


Jewellery made from crystal



Decorative item made from crystal

Raw crystal