Utilization of Calcium Carbonate (Clam Shell)

Hsu Mon Phyo[1], Aye Aye Mar[2]

Abstract

The clam shells (*Mercenaria mercenaria*) were ground and sieved with (-150+200mesh) screen. The elemental compositions of clam shells powder were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) method. In this research work, calcium chloride, calcium sulphate dihydrate (gypsum) and calcium sulphate hemihydrate (plaster of paris) were prepared from clam shells powder. Determination of the optimum conditions for the conversion of clam shell to calcium chloride, calcium sulphate dihydrate and calcium sulphate hemihydrate were conducted using different parameters such as various amount of acids, reaction times and temperatures and also various salting-out agents. The compounds and elemental compositions of prepared calcium chloride, calcium sulphate dihydrate and calcium sulphate hemihydrates were determined and compared with that of the commercial products.

Key words: clam shells, gypsum, plaster of paris, EDXRF method

Introduction

The clam shell (*Mercenaria mercenaria)* is a clam or bivalve mollusc in the family *Veneridae*. It is distributed worldwide and due to its ecological and economic interest has been proposed as a bioindicator. The hard clam (*Mercenaria mercenaria*), also known as a quahog (or quahaug), round clam, or hard-shell clam, is an edible marine bivalve mollusk which is native to the eastern shores of North America, from Prince Edward Island to the Yucatan Peninsula. (Wekipedia, the free encyclopedia)

Calcium carbonate ($CaCO_3$) is naturally available in the form of rocks and minerals. Its most common natural forms are chalk, limestone, and marble, produced by the sedimentation of the shells of small fossilized snails, shellfish, and coral over millions of years. Eggshells and seashells are calcium carbonate. Calcium chloride ($CaCl_2$) is traditionally prepared by dissolving marble chips or limestone chips in hydrochloric acid.

Calcium sulphate ($CaSO_4$) can be obtained from natural rock mines or by chemical synthesis. On the basis of amount of crystal water, calcium

[1] MSc Student, Department of Industrial Chemistry, University of Yangon

[2] Lecturer, Dr., Department of Industrial Chemistry, University of Yangon

sulphate can be classified as calcium sulphate dihydrate ($CaSO_4.2H_2O$, gypsum), calcium sulphate hemihydrate ($CaSO_4.{}^1/_2H_2O$, plaster of paris) and anhydrite calcium sulphate ($CaSO_4$). In the preparation of calcium sulphate dihydrate, salting-out method was used. This method yields the sulphate salts by the addition of acetone or sodium chloride to the acid reaction mixture.

The calcination process is important in the transformation of gypsum to plaster of paris. Plaster of paris is the result of calcining the gypsum, commercially; the gypsum is first ground and then subjected to temperature of certain value. The calcination temperature is different by different gypsum used, purity and processes. During this period, part of the water of crystallization is driven off. Depending on varying the degree of calcinations, the different grates of gypsum products are obtained, namely first settle stucco or plaster of paris which is calcium sulphate hemihydrate, $CaSO_4{}^1/_2H_2O$ and second-settle stucco or anhydrite $CaSO_4$.

The aims of this research work are to utilize the clam shells in the preparation of calcium chloride, calcium sulphate dihydrate (gypsum), calcium sulphate hemihydrates (plaster of paris), to evaluate the suitable procedure and specific characteristics of calcium chloride, calcium sulphate dihydrate and calcium sulphate hemihydrates.

Materials and Methods

Materials

In this research work, waste clam shells were obtained from Shwe Thandar Co. Ltd., South Dagon Industrial Zone, Yangon Region. Calcium carbonate, calcium chloride, calcium sulphate dihydrate, hydrochloric acid, acetone and sulphuric acid (analar grade, British Drug House Co. Ltd., England) were used.

Methods

Preliminary Preparation of Clam Shells

Initially, clam shells were washed with water to remove the adhering dirt and then dried. 1000 g of dried clam shells were ground in an grinder for 30 min and screened by using Tyler screen of 150 and 200 mesh size.

Analysis of Clam Shells Powder

Clam shells powder was analyzed by Energy Dispersive X-Ray Fluorescence **(E**DXRF) method (Spectrometer, model EDX-700).

Preparation of Calcium Chloride

10 g of (-150 + 200) mesh size clam shells powder and 100 ml of (1.5 N) hydrochloric acid were placed into the beaker and stirred. The mixture was filtered and the filtrate was heated on a sand bath at 150˚C for 40 min. During heating, the amorphorous calcium chloride salt was obtained and cooled to room temperature.

Optimization and Characterization of Calcium Chloride

The Effect of Strength of Hydrochloric Acid Solution

In the preparation of calcium chloride, the effect of the strength of hydrochloric acid solution on yield of calcium chloride was determined. About 10g of clam shells powder was reacted with each of 100 ml of different strengths of hydrochloric acid solution such as 1.5 N, 1.9 N, 2.3 N, 2.7 N and 3.1 N respectively.

The Effect of Heating Time

In the preparation of calcium chloride, the effect of heating time on yield of calcium chloride was determined using the reaction temperature at 150˚C for each of reaction times such as 30 min, 40 min, 50 min, 60 min and 70 min respectively.

Determination of the Elemental Compositions

The elemental compositions of prepared calcium chloride and commercial calcium chloride were analyzed using Energy Dispersive X-Ray Fluorescence (EDXRF) method and their analysis data were recorded.

Preparation of Calcium Sulphate Dihydrate (Gypsum)

15g of (-150+200 mesh size) clam shells powder and 100ml of distilled water were placed into the beaker. The contents were stirred constantly while 33ml of (20˚Bé, 12.1 N) hydrochloric acid solution was added portion wise over a period of 5 min. When the clam shells powder was completely soluble, 7ml of (66˚ Bé,36 N) sulphuric acid solution and 17 ml of distilled water were added by drop wise manner into the slurry

within 10 min and stirred. Finally, 50ml of acetone as salting-out agent was added into the slurry within 5 min. The mixture was heated at 100˚C for 30 min to precipitate the dissolved calcium sulphate dihydrate and then dried in an oven at 90˚ C for an hour. The prepared calcium sulphate dihydrate was cooled to room temperature and weighed.

The above procedure was repeated for the preparation of calcium sulphate dihydrate except 0.7g NaCl as salting-out agent and also conducted without salting-out agents.

Optimization and Characterization of Calcium Sulphate Dihydrate (Gypsum)

The Effect of Amount of Sulphuric Acid

In the preparation of calcium sulphate dihydrate, the effect of amount of sulphuric acid on yield of calcium sulphate dihydrate was determined using different amounts of (36 N) sulphuric acid solution such as 7ml, 8ml, 9ml, 10ml and 11 ml while the amount of other compounds were fixed.

The Effect of Salting-out Agent

The effect of salting-out agent on yield and appearance of calcium sulphate dihydrate was determined with different salting-out agents such as acetone, sodium chloride and also conducted without salting-out agents.

Determination of the Chemical Compositions

Elemental compositions of prepared calcium sulphate dihydrate and commercial product were analysed using Energy Dispersive X-Ray Fluorescence (EDXRF) method and their analysis data were recorded.

The free water and combined water in prepared calcium sulphate dihydrate and commercial samples were determined.

Determination of Solubility

5g of prepared calcium suphate dihydrate and 10ml of each of different solvents such as water, ethanol and dilute hydrochloric acid solution were added into the conical flask and stirred constantly. During stirring, the solubility nature of prepared calcium sulphate dihydrate was observed at the time interval of 15 minutes.

The above procedure was repeated for the commercial calcium sulphate dihydrates and their respective results were recorded.

Purification of Prepared Calcium Sulphate Dihydrate

10 g of prepared calcium sulphate dihydrate and 20ml of distilled water were added into the conical flask and continuous stirring with a glass-rod for 15min.Then, light insoluble impurities floated on the water surface were decanted and the solution was filtered. The residual calcium sulphate dihydrate was dried in an oven at 90˚C for an hour and cooled to room temperature and weighed again. The physical properties of purified calcium sulphate dihydrate were observed and recorded.

The above procedure was conducted for second and third time washings of calcium sulphate dihydrate and the results are recorded.

Preparation of Calcium Sulphate Hemihydrate (Plaster of Paris)

Firstly, the prepared calcium sulphate dihydrate was ground and sieved using 150 and 200 mesh size screen. Then, 5g of calcium sulphate dihydrate (-150 + 200 mesh size) was placed in a stainless steel plate and spread out in thin layer. Then, the stainless steel plate was placed in an oven and heated at a temperature range of 100˚C to 150˚C for an hour and weighed.

The above procedure was repeated using commercial calcium sulphate dihydrate to convert the calcium sulphate hemihydrate.

Characterization of Prepared Calcium Sulphate Hemihydrate
Determination of Combined Water

The percentrages of combined water in prepared and commercial samples of calcium sulphate hemihydrate and were calculated as follows.

$$CaSO_4.2H_2O \xrightarrow{\blacktriangle} CaSO_4\,{}^1/_2\,H_2O + {}^3/_2\,H_2O$$

172.2g/ mol (at 110 -150˚C for an hour) 165.14g/mol 27 g/mol

Determination of Elemental Compositions

Elemental compositions of prepared samples of calcium sulphate hemihydrate from clam shell and commercial calcium sulphate dihydrate were analyzed using Energy Dispersive X-Ray Fluorescence (EDXRF) method. The analyses data were compared.

Results and Discussion

In this research work, clam shells powder was analyzed by Energy Dispersive X-Ray Fluorescence (EDXRF) method and the results are shown in Table (1). It was found that 97.33%w/w of calcium, 1.042%w/w of potassium and 1.029%w/w of strontium were present in clam shells powder.

For the preparation of calcium chloride, the effect of strength of hydrochloric acid solution and the effect of heating time on yield percent of calcium chloride were studied. The results in Tables (2) and (3) show that 90.91%w/w of calcium chloride were obtained at 150ºC for 50 min using 2.7N of hydrochloric acid solution.

The elemental compositions of prepared and commercial samples of calcium chloride were determined by using Energy Dispersive X-Ray Fluorescence (EDXRF) method. From the results in Table (4), it can be seen that the major constituents such as 32.971%w/w of calcium and 61.658%w/w of chloride in prepared calcium chloride that are agreement with the commercial product.

The results in Tables (5) to (8) indicate that the good yield percent of calcium sulphate dihydrate was found using 15g clam shells powder, 33ml of (12.1N) HCl solution, 9 ml of (36N) H_2SO_4 solution and 50 ml of acetone as salting-out agent at 100ºC for 30 min.

The solubility of prepared and commercial calcium sulphate dihydrate samples were determined and the results are shown in Table (10). It can be seen that the solubility of both samples are fairly close to each other. The prepared calcium sulphate dihydrate was purified with water and the results are shown in Table (11). The results show that second times of washing gave the whiter colour of purified calcium sulphate dihydrate.

In the preparation of calcium sulphate hemihydrate, the effect of dehydration temperature on weight loss of calcium sulphate dihydrate was studied. The results in Table (12) indicate that the total weight loss for prepared calcium sulphate dihydrate was 74.14 %w/w whereas total weight loss of commercial sample was 74.61%w/w respectively.

The elemental compositions and combined water of prepared calcium sulphate hemihydrate were determined and the results are shown in Table (13). The results in Table (13) indicate that 56.065%w/w of calcium and 43.136%w/w of sulphur content in prepared calcium sulphate hemihydrate whereas 53.841%w/w of calcium and 40.140%w/w of sulphur content in commercial product.

Table (1) Elemental Composition of Clam Shells Powder and Commercial Calcium Carbonate

Sr. No.	Elements	Compositions, (%w/w)	
		Clam Shells	Calcium Carbonate
1	Calcium, (Ca)	97.333	96.821
2	Potassium, (K)	1.042	1.345
3	Iron, (Fe)	0.596	0.430
4	Strontium,(Sr)	1.029	1.304

The results were determined at Universities' Research Center, Yangon University

Table (2) Effect of the Strength of Hydrochloric Acid on Yield Percent of Calcium Chloride

Sample No.	Ingredients			Reaction Condition		Yield of $CaCl_2$
	Clam Shell Powder (g)	Strength of HCl (N)	HCl Solution (ml)	Temp. (°C)	Time (min)	(%w/w)
I	10	1.5	100	150	40	60.03
II	10	1.9	100	150	40	65.58
III	10	2.3	100	150	40	73.20
IV*	10	2.7*	100	150	40	82.73
V	10	3.1	100	150	40	83.54

* Suitable strength of HCl

Table(3) Effect of Heating Time on Yield Percent of Calcium Chloride
Heating temperature = 150°C

Sample No.	Clam Shell Powder (g)	HCl solution (ml)	Strength of HCl (N)	Heating Time (min)	$CaCl_2$	
					(g)	(%w/w)
I	10	100	2.7	30	8.20	74.55
II	10	100	2.7	40	9.10	82.73
III*	10	100	2.7	50*	10.00	90.91
IV	10	100	2.7	60	10.00	90.91
V	10	100	2.7	70	10.00	90.91

* Suitable heating time

Table (4) Elemental Compositions of Prepared Calcium Chloride and Commercial Calcium Chloride

No.	Sample	Compositions of Elements, (%w/w)							
		Ca	Cl	Sr	S	P	Cu	Fe	Mn
I	Commercial $CaCl_2$	32.46	63.98	0.03	0.98	2.51	-	-	-
II*	Prepared $CaCl_2$ (2.7 N HCl used)	32.97	61.66	0.24	1.94	3.06	0.04	0.09	-
III	Prepared $CaCl_2$ (1.5 N HCl used)	48.53	44.29	0.92	-	4.75	0.23	0.99	0.28

*The most suitable prepared $CaCl_2$
The results were determined at Universities' Research Center, University of Yangon

Table (5) Effect of Amount of Sulphuric Acid on Yield of Calcium Sulphate Dihydrate

Reaction temperature = 100ºC
Reaction time = 30 min
Salting - out agent = Acetone

Sample No.	Ingredients				H_2SO_4 Solution		Yield of $CaSO_4.2H_2O$ (g)
	Clam Shells (g)	12.1N HCl (ml)	H_2O (ml)	Acetone (ml)	36N H_2SO_4 (ml)	H_2O (ml)	
I	15	33.00	100	50	7	17	15.35
II	15	33.00	100	50	8	17	17.37
III*	15	33.00	100	50	9*	17	25.80
IV	15	33.00	100	50	10	17	25.85
V	15	33.00	100	50	11	17	25.87

* Suitable amount of H_2SO_4

Table (6) Effect of Amount of Sulphuric Acid on Yield of Calcium Sulphate Dihydrate

Reaction temperature = 100ºC
Reaction time = 30 min
Salting - out agent = Sodium chloride

Sample No.	Ingredients				H_2SO_4Solution		Yield of $CaSO_4.2H_2O$ (g)
	Clam Shells (g)	12.1N HCl (ml)	H_2O (ml)	NaCl (g)	36N H_2SO_4 (ml)	H_2O (ml)	
I	15	33.00	100	0.7	7	17	18.08
II	15	33.00	100	0.7	8	17	18.04
III*	15	33.00	100	0.7	9*	17	20.60
IV	15	33.00	100	0.7	10	17	19.29
V	15	33.00	100	0.7	11	17	19.25

* Suitable amount of H_2SO_4

Table (7) Effect of Amount of Sulphuric Acid on Yield of Calcium Sulphate Dihydrate

Reaction temperature = 100ºC
Reaction time = 30 min
Salting - out agent was not used in precipitation.

Sample No.	Ingredients			H_2SO_4 Solution		Yield of $CaSO_4.2H_2O$ (g)
	Clam Shells (g)	12.1N HCl (ml)	H_2O (ml)	36N H_2SO_4 (ml)	H_2O (ml)	
I	15	33.00	100	7	17	15.38
II	15	33.00	100	8	17	18.39
III*	15	33.00	100	9*	17	21.30
IV	15	33.00	100	10	17	19.36
V	15	33.00	100	11	17	19.28

* Suitable amount of H_2SO_4

Table (8) Comparison of the Yield and Colour of Prepared Calcium Sulphate Dihydrate

Reaction temperature = 100ºC
Reaction time = 30 min

Sample No.	Ingredients			H_2SO_4Solution		Yield of $CaSO_4.2H_2O$ (%w/w)	Colour
	Clam Shell (g)	12.1N HCl (ml)	H_2O (ml)	36N H_2SO_4 (ml)	Water (ml)		
I*	15	33.00	100	9	17	25.80	Gray
II	15	33.00	100	9	17	20.60	Pale yellow
III	15	33.00	100	9	17	21.30	Yellow

* Suitable sample
Sample I = Using of acetone as salting-out agent
Sample II = Using of NaCl as salting-out agent
Sample III = Without salting - out agent

Table (9) Compositions of Prepared and Commercial Samples of Calcium Sulphate Dihydrate

Sr. No.	Constituents	Compositions, (%w/w)	
		Prepared * $CaSO_4.2H_2O$	Commercial $CaSO_4.2H_2O$
1	Calcium (Ca)**	65.316	61.303
2	Sulphur (S)**	33.978	38.639
3	Strontium (Sr)**	0.706	0.058
4	Free Water	0.210	0.190
5	Combined Water	20.16	20.020

* Prepared sample using acetone as salting-out agent

** The results were determined at Universities' Research Center, University of Yangon

Table (10) Comparison of the Solubility of Prepared and Commercial Samples of Calcium Sulphate Dihydrate

Sr. No.	$CaSO_4$ $2H_2O$ (g)	Solvents		Prepared * $CaSO_4.2H_2O$		Commercial $CaSO_4.2H_2O$	
		Type	(ml)	Inference	Soluble (%w/w)	Inference	Soluble (%w/w)
1	5	H_2O	10	slightly soluble	0.23	slightly soluble	0.25
2	5	C_2H_5OH	10	insoluble	-	insoluble	-
3	5	HCl (dil)	10	insoluble	-	insoluble	-

*Prepared sample using acetone as salting-out agent

Table (11) Effect of Washing Time on the Colour of Calcium Sulphate Dihydrate Samples

Sample No.	$CaSO_4$ $2H_2O$ (g)	H_2O (ml)	Washing Time	Purified $CaSO_4.2H_2O$ (g)	Colour of Pure Sample	Remarks (after washing)
I	10	-	-	-	Gray	Impure
II	10	20	1^{st}	9.65	Gray	Pure
III*	10	20	2^{nd}	9.57	White	Pure
IV	10	20	3^{rd}	9.56	White	Pure

*Suitable washing time

Table (12) Effect of Dehydration Temperature on Weight Loss of Calcium Sulphate Dihydrate

Amount of sample = 5g,
Heating time = 1hr

Sample	Weight Loss, (g)					Total Weight Loss	
	110°C	120°C	130°C	140°C	150°C	(g)	%w/w
Prepared Sample	0.078	0.077	0.158	0.169	0.255	0.737	70.5
Commercial Sample	0.082	0.078	0.160	0.165	0.259	0.745	71.28

Table (13) Chemical Compositions of Prepared Calcium Sulphate Hemihydrate

Sr. No.	Constituents	Compositions of $CaSO_4.½H_2O$, (%w/w)	
		Prepared Sample	Commercial Sample
1	Calcium, (Ca)	56.065	53.841
2	Sulphur, (S)	43.136	40.140
3	Strontium, (Sr)	0.537	3.007
4	Copper, (Cu)	0.059	1.009
5	Iron, (Fe)	0.203	2.003
6	Combined water	5.126	5.007

The experiments were conducted at Universities' Research Center, University of Yangon



Figure (1) Clam Shells



Figure (2) Prepared Calcium Chloride



Figure (3) Commercial Calcium Chloride



Figure (4) Prepared Calcium Sulphate Dihydrate



Figure (5) Commercial Calcium Sulphate Dihydrate



Figure (5) Calcium Sulphate Hemihydrate

Sample I = Commercial Calcium Sulphate Hemihydrate

Sample II = Prepared Calcium Sulphate Hemihydrate

Conclusions

In this research work, the waste clam shells were utilized in the preparation of $CaCl_2$, $CaSO_4.2H_2O$ and $CaSO_4.½H_2O$. The chemical compositions of prepared $CaCl_2$, $CaSO_4.2H_2O$ and $CaSO_4.½H_2O$ were agreement with those values from the commercial products. Therefore, waste clam shells powder can be used in the preparation of $CaCl_2$, $CaSO_4.2H_2O$ (gypsum) and $CaSO_4.½H_2O$ (plaster of paris).

Acknowledgements

We would like to express our deepest gratitude to Dr Khin Thet Ni, Professor and Head of Industrial Chemistry Department, University of Yangon for giving permission to perform this research at the Department of Industrial Chemistry.

We would like to express our special thanks to Dr. Than Htaik, Director General (Retd), Cottage Industries Department, Ministry of Co-operative, for his kind encouragement, guidance and numerous invaluable suggestions.

References

American Chemical Society, (2006), Reagent chemicals: specifications and procedures: American Chemical Society Purifications, Official from January,Oxford University Press.

Benchtop Powder XRD Low-cost X-ray Diffraction System Quantitative Phase & Crystallinity. www.rigaku.com

FAO Species Identification and Data Programme (SIDP)-Fisheries and Aquaculture Department.

Kirk-Othmer, (1978), Encyclopedia of Chemical Technology, Vol-24, 3th Edition, John Wiley and Sons Inc. New York.

Poppe, G. T. and Goto, Y., (1991), European Seashells.Vol-1, ChristaHemmen.

Zumdahl, Steven S.,(2009), Chemical Principles, 6th Edition, Houghton Mifflin Company. p. A2:

Website

http://answers.ask.com/science/chemistry/what is acetone used for. Harte,

http://www.how.com/how8019263produce-gypsum.Htmlixzzlgxip8zTK.

http://www.livestrong.com/article/278802-hydrochloric-acid-calcium-hydroxide/ixzz1ftG55F4w

http://www.wiki.org/calcium-chloride/wiki

http://www.wiki.org/clamshell/wiki