1928

Cone deformation eutectics using sodium chloride, dolomite, and alpite rock

William K. Schweickhardt

CONE DEFORMATION EUTECTICS
USING
SODIUM CHLORIDE, DOLOMITE, AND APLITE ROCK.

A Thesis Presented for the Degree of Bachelor
of Science in Ceramic Technology

-by-

William
W. K. Schweickhardt.

MISSOURI SCHOOL OF MINES AND METALLURGY
1928.

Approved by,

ACKNOWLEDGEMENT

Throughout the work on this thesis, many suggestions and much guidance has been given by Professor C. M. Dodd, for which the writer wishes at this time to thank him.

Cone Deformation Eutectics, Using Sodium Chloride, Dolomite, and Aplite Rock.

Introduction.

Heterogeneous Equilibrium, alone, is an extensive study in itself and no discussion of it will be given here. It is known from this study that different phases are formed in various systems, the system consisting of two or more components. Some systems form an eutectic, which is a mixture of two solids which combine to form a liquid at a lower degree of temperature than either of the melting points of the two solids, as shown in the two component system of KCl and LiCl[1]; some systems form solid solutions in which there is no eutectic formed, and the solids deposit in no definite proportions, as in the two component system of Cu and Ni[1]. There are many systems in which more complicated conditions occur, however, the most widely known system is that one which forms an "eutectic".

Object of Research.

The purpose of this problem is to find, if possible, an eutectic mixture existing between Dolomite ($CaCO_3 . MgCO_3$) and salt (NaCl). The above eutectic being found, it is

[1] Millard, Physical Chemistry for Colleges Page 309.

of a further purpose to find an eutectic mixture between the eutectic found in the system Dolomite-Sodium Chloride and Aplite. The scope of this study does not go beyond a two component eutectic mixture.

Outline of Proceedure.

1. A binary system of eleven members, having as its end members, one hundred per cent Dolomite and one hundred percent sodium chloride, will be used to locate, approximately the cone deformation eutectic. After the cone deformation eutectic has been approximately found, another series of any number of members required to locate the cone deformation eutectic definitely will be made. The materials will be ground, separately, to pass a 60 mesh sieve, proportioned by weight, and then mixed by hand on a mixing cloth. Sufficient dextrine solution will be added to form a good bond. Five cones will be made of each member, the cones being hand made using a standard cone mold to mold them. The cones will be dried on a pallet, and placed in numbered sections to distinguish the cones from one another. After they are dried, they will be set in cone placques consisting of fifty percent Georgia Kaolin and fifty percent Alumina, dried, and fired in a Hoskins Electric Muffle. The temperature will be determined by the use of a base metal (Chromel-Alumel) thermocouple which is attached to a Leeds-Northrup Potentiometer, using a cold junction for compensation. The first binary system will be known

as I_x, the second binary system as II_x, the third binary system as III_x, with x designating the cones from one another in the systems.

2. Another binary system of eleven members will then be made up with one hundred percent Aplite and one hundred precent II_x as end members. II_x will be the cone deformation eutectic as found in the system Dolomite-Sodium Chloride. An approximate cone deformation eutectic will be found, then a second system will be made up of any number of members required to give a definite cone deformation eutectic. The drying and firing and placing in the cone placques will be the same as discussed in the previous paragraph. These systems will be known as III_x and IV_x.

When a new series is to be made up, in which a member of the previous series is to be used, new mixtures by weight, will be prepared.

Definition of the term "Cone Deformation Eutectic"

A term substituted for eutectic and eutectic mixture, since the ingredients of the cone, i.e., the components of the system, are not fused, but due to a catalytic or fluxing agent, cause the cone to deform at a lower temperature than the end members deform without a eutectic being formed.

Materials.

The sodium chloride used is commercially pure sodium chloride containing one percent Calcium Phosphate to prevent caking. The Calcium oxide formed from the decomposition of the Calcium Phosphate in heating, is not enough to take into consideration in calculating the members of the binary systems, i.e., calculating the composition of the members. The amount of Calcium oxide formed is 0.17 grams Calcium oxide to every 100 grams Sodium Chloride used.

The Aplite rock is found in deposits owned by the Gordon White Brick Co., at Gordon Georgia. No chemical analysis of this aplite rock is available. However, it is known that the aplite is of inferior quality containing many impurities and a high percentage of iron. This fact is known from observation, since this aplite is of a dirty brown color, as compared with a pure aplite which has a greyish green color.

The Dolomite used was obtained from the Jefferson City (Ordovician) formation near Rolla, Mo. The sample may have been subjected to some weathering since the sample was taken from a stratum at the entrance of a limestone drift mine. No chemical analysis of this rock is available, but from previous analysis of Dolomite from this stratum, it was found to contain approximately fifty one percent Calcium Carbonate and forty-one percent Magnesium Carbonate.

It is hoped that the sodium chloride will react with the Fe_2O_3 in the aplite, forming volatile chlorides which will pass off as a gas.

Method of Proceedure for
Cone Deformation Eutectic Between Dolomite and Sodium Chlorid

The Dolomite and sodium chloride were groung separately to pass through a 60 mesh sieve. An eleven member binary system was made up to determine the amount of each substance used. The end members consisted of one hundred percent Dolomite and one hundred percent Sodium Chloride respectively.

TABLE I

Composition of Series I.

Member No.	1	2	3	4	5	6	7	8	9	10	11
Dolomite %	0	10	20	30	40	50	60	70	80	90	100
NaCl %	100	90	80	70	60	50	40	30	20	10	0

This series consisted of members of teh percent variations, the purpose being to approximate the cone deformation eutectic.

The cones were made up as previously described, dried and then placed in cone placques. Two cone placques were made, the first placque containing members one to five inclusive, the second placque containing members six to eleven inclusive. The cone placques were then dried and fired. The rate of heating was the maximum of the furnace which is about 20 degrees Centigrade per minute. until 650 degrees Centigrade was reached. At this point enough resistance was cut in so that the temperature rise approximated 5 degrees Centigrade per minute. No evidence of any deformation of the cones was noticed until about 775 degrees Centigrade when cones 3 and 4 began to deform.

TABLE II

Deformation Data on Series I.

Member No.	1	2	3	4	5	6	7	8	9	10	11
Deformation Temp. °C.	808	---	780	780	828	Temperature not obtained.					

Discussion of Data.

Sodium Chloride melts at 805 degrees Centigrade. The data obtained in this run for the fusion point of sodium chloride was 808 degrees Centigrade which is a comparitively good check. The run was not continued beyond cone 5, since the desired information was obtained. This run showed that there is a deformation eutectic formed between Dolomite and Sodium Chloride and that is lies somewhere between members 2 and 5. Since ~~member~~ cone 3 and 4 came down almost simultaneously, cone 3 preceding cone 4 by a fraction of a second, it was the opinion that cone 3 lies on one side of the cone deformation eutectic point and cone 4 on the other. Therefore a series of cones ranging from members I_2 to I_5 were made up to ascertain the cone deformation eutectic. Intermediate cones, one between members I_2 and I_3, and one between members I_4 and I_5 were made. An eleven member binary system was made up between members I_3 and I_4

using I_3 and I_4 as end members.

TABLE III

Composition of Series II.

Member No.	% NaCl	% Dolomite.
I_2	90	10
1	85	15
I_3	80	20
2	79	21
3	78	22
4	77	23
5	76	24
6	75	25
7	74	26
8	73	27
9	72	28
10	71	29
I_4	70	30
11	65	35
I_5	60	40

Two cone placques were made, the cones placed in them, dried and fired. In this run the full capacity of the furnace was used only until 500 degrees Centigrade was obtained, in order to have a longer of slow heat treatment. At 500 degrees Centigrade the rate of heating was decreased to 10 degrees Centigrade a minute until 600 Degrees Centigrade was reached. At this temperature, the rate of heating was reduced to 5 degrees Centigrade per minute and held there through the remainder of the run.

TABLE IV

Deformation data on Series II.

Member No.	Deformation temp. Degrees Cent.
I_2	No Record
1	No Record
I_3	765
2	765
3	765
4	765
5	760
6	765
7	766
8	Broke at base.
9	767
10	767
I_4	768
11	No record
I_5	No record.

Discussion of Data.

At 750 degrees Cent. Member 8 started to deform but broke at the base. At 756 degrees Cent. members 5, 10, 11, started to deform. At 760 degrees Cent. cone II_5 (Table IV) was completely deformed. Also members I_3, II_2, II_3, II_4, and II_6 Started to deform and were completely deformed at

765 degrees Centigrade. These members came down in rapid succession, seemingly member II_4 coming down first. No check was made on these members since the cone deformation eutectic was all that was desired. At 766 degrees Cent. member II_7 came down, and at 767 degrees Cent. Members II_9 and II_{10} were down. Member I_4 came down at 768 degrees Cent. No records of Members I_2, II_1, II_{11}, and I_5 were obtained since they were seen to be out of the desired range.

Note of Error in the Above Proceedure.

The Dolomite used in the cones was crushed by crushing rolls to pass through a 10 mesh sieve. The fines of this were taken and passed through a 60 mesh sieve, thereby introducing the possible error that since the entire sample was not taken and only the fines were taken, the proper amount of the harder particles, such as quartz, would be lacking in the fines, i.e., in the proper amount, which would probably cause the cones to come down at a lower temperature than if the entire sample would have been passed through a 60 mesh sieve, since quartz has a higher fusing temperature than the carbonates of Calcium and Magnesium. Time would not permit to make up a new sample of Dolomite.

The aplite used in the next step was quartered and the entire sample, groung in a Brown Pulverizer, passed through a 60 mesh sieve. The same dolomite sample that was used in series I and II is used in the next operation.

Method of proceedure for a Cone Deformation Eutectic between Member II_5 and Aplite.

A binary system of eleven members, having as its end members, one hundred per cent member II_5 and Aplite, respectively, was made up.

TABLE V.

Composition of Series III.

Member No.	%Member II_5	% Aplite.
II_5	100	0
2	90	10
3	80	20
4	70	30
5	60	40
6	50	50
7	40	60
8	30	70
9	20	80
10	10	90
11	0	100

These mixtures were mixed in a mortar and not on a mixing cloth. The cones were made as previously described, dried, placed in cone plaques which were dried and fired in the same manner as in the previous runs. No record of heat treatment was kept until 500 degrees Cent. was reached, the furnace being operated at full capacity to this point. At this temperature, the rate of heating was reduced to approximately 10 degrees per minute. At 650 degrees Cent. the rate of heating was farther reduced to 7 degrees per minute and at 700 degrees Cent., it was again reduced to 5 degrees per minute.

No data was obtained since no cone deformation eutectic was found in this system which was lower than the cone deformation temperature of member II_5. No deformation whatsoever was noticed until 775 degrees C. when member III_1 began to deform and was completely deformed at 779 degrees C. At 786 degrees Cent. member III_2 was fully deformed. The temperature was raised to 1000 degrees Centigrade but no further deformations were observed. At 1000 degrees C. member III_3 began to deform but did not deform completely. It was not necessary to continue the operation any longer since no cone deformation eutectic was formed. The operation was, however, continued long enough to see that the cones were deforming in consecutive order which strongly indicates a solid solution.

Conclusion.

1. From Series II, it was found that there is a cone deformation eutectic formed between sodium chloride and Dolomite, the percentages being ax seventy-six percent Sodium Chloride and twenty-four percent Dolomite. The cone deformation eutectic temperature was found to be 760 degrees Centigrade, a temperature lower than that of

the fusion of pure salt or dolomite.

2. It was hoped that there would be a cone deformation eutectic or a eutectic found in Series III, but such was not the case. Only a solid solution resulted.

There is a discrepancy of 19 degrees C. in regards to the cone deformation eutectic temperature of Cone II_5 between Series II and III, Series II giving member II_5 a cone deformation eutectic temperature of 760 degrees C. and Series III giving member II_5 a cone deformation eutectic temperature of 779 degrees C. This is more than likely due to the fact that the protection tube of the thermocouple was broken in run III where the two wires are coupled, therby eliminating the heat absorption through the protection tube which was had in run II. The protection tube being broken allowed the heat to come in direct contact with the couple, thereby boosting the temperature of the cone deformation eutectic in series III.

Some of the residue of the cones after firing was placed under the microscope, No fusion was seen, and a crystalline substance was seen instead of a fused mass. These crystals were probably those of Calcium Carbonate since the carbonates of Calcium do not decompose until 825 degrees C. and this temperature was not reached when firing the cones from which this sample was taken. Therefore it is seen that no real eutectic is formed, but more than likely the sodium chloride acts as a flux on the Dolomite causing the cone to deform as a standard pyrometric cone deforms, without a eutectic being formed.

Application to Industry.

From the above data it can be seen that a flux is obtained. This flux may be used to reduce the vitrification point of clay bodies that have a high vitrification point. It will also form chlorides, due to the presence of the sodium chloride, which are volatile, and which will aid in removing the undesirable impurities in the body. It may be used in enamels and glazes to reduce the temperature required in firing them. It may be used wherever a flux is needed or desired, depending upon the physical properties desired.

Recommendations for Further Research.

A further study can be made by determining how much of the sodium chloride and Dolomite cone deformation eutectic, together with an addition aplite will be required to give the best results in lowering the vitrification point of any body. Also, since aplite is a flux in itself, a binary system of one hundred percent clay body and one hundred per cent aplite as end members, could be made up and the physical properties of these members studied.
In order to use the flux, obtained in this work, the most probable line to follow would be to form a triaxial system, using one hundred percent clay body, one hundred percent aplite, and one hundred per cent of member II_5 as end members, and then make physical tests on these members. The size of the triaxial depends upon the requirements

of the physical tests which are to be made upon the body. A mixture of various clays can be used to make uptthe clay body which is used for one end member.