THE SYSTEM OF GELLED FOAM OF CLAY-IN-WATER SUSPENSION FOR THE PREPARATION OF LIGHTWEIGHT INSULATING REFRACTORY

Part I. Formation and Gelling of Clay-Based Foam.

BY;

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Summary :

Under neutral conditions colloidal plates of clay in water are negatively charged. When the pH of the clay-in-water dispersion is lowered slightly, positive charges can develop on the edges of the clay plates giving rise to an edge-to-face type gelation. Sodium fluosilicate, which has a rather high acidity and which is very slightly soluble in water, can be used as gelling agent. By beating a clay slip containing a surfaceactive agent "Teepool" and sodium fluosilicate, one can obtain a stable foam followed by formation of a firm gel. When then the wet gel is dried a solid foam product is built-up.

I. Introduction.

In most industrial processes foam formation causes desirable or undesirable problems. In undesirable cases the formation of foam must be prevented or destructed, as is applied in water boilers, leather tanning, latex dipping processes etc. On the other hand one must promote foam formation for example in fire fighting mixture, soap solution, in ore flotation and in the manufacture of foam products like bread, foam rubber and plastic sponges.

Foam products are made for divergent purposes. In case of foam refractory, its high porosity is wanted for a good thermal insulation.

The effect of porosity on thermal conductivity has received a good deal of attention in recent years, viz. it was shown that the larger the porosity the smaller the value of the thermal conductivity. [1]

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The common method of producing pores in a fire clay product is to introduce to the plastic clay mix an organic material that later on can be burned out to leave holes in the brick. Ground wood, cork and other material of the same type are usually added to the plastic clay. So does the brick maker in Java, who adds excrements of buffalo to the clay slip up to now.

MANDELL [2]) added flakes of naphthalene to the clay mix, that when later on the ware is dried at high temperature, the naphthalene can be sublimed, and leaving pores in the dried clay product.

Introducing into the clay, bubbles of gas by chemical reaction as was introduced by ERICSON [3]), that are sufficiently stable to remain in the mix until the material is dried and burned, one can obtain porous clay ware. In this process, shale ashes, lime and metals such as Zn or Al were adapted to react with the other ingredients to generate gas when water is added [4]).

ERICSON [5]) and ROOS [6]) obtained products having considerable stability by mixing a preformed foam into the clay slip.

Still another method was introduced by MOCHEL [7]), who made bubbles in a sticky solution first, and then adding the refractory powder to the mixture.

Coalescing of individual bubbles into larger ones can be more or less prevented by adding to the clay mix, a setting agent e.g. gypsum plaster as was done by HUSAIN and BOLE [8]).

All the above mentioned processes were patented in the U.S.A.

The present investigation of the author will show that it is possible to get a stable foam by beating a clay slip in the presence of a gelling agent, viz. sodium fluosilicate. Used as foaming agent was a solution of "Teepol", a secondary sodium alkyl sulphate [9]), a detergent made by the Shell Chemical Co.

II. **Formation of clay-based foam.**

1. Colloid Chemical Theory of Foam Systems.

   a. Foam system.

   A foam can be considered as a type of emulsion, in which the inner phase is a gas, usually air. In agreement with the concept that colloid systems are dispersed systems, in which at least one dimension of one phase is very small [10]), a foam can thus be placed on the list of colloid systems.

In foam brick the dispersed phase consists of bubbles of air, which are dispersed throughout the continuous solid clay phase. Such a solid foam is formed by introducing air in a clay slip and afterwards allowing the water to evaporate.

In consequence of foaming phenomenon, the interface between the water containing the clay particles and the air are increased enormously than beforehand.

Due to the existence of the so called surface tension of the water, energy is required to generate an increase in surface area of the liquid.

b. Surface tension.

Surfase tension arises from a tendency of a liquid to reduce its surface to a minimum resulting from the attraction forces which tend to pull the surface molecules into the interior, and is measured in an atmosphere saturated with the liquid vapour [11]).

Surface tension is usually denoted by the symbol γ and is numerically equal to the work necessary on creating a unit area of new surface.

In the basic thermodynamic function:

$$dU = \delta Q + \delta W + \mu dv \tag{1}$$

the quantity of work done δw, for a liquid-gas interface which undergoes extension of its area, can be replaced by γdA, so we obtain

$$dU = \delta Q + \gamma dA + \mu dv \tag{2}$$

or because

$$\delta Q = TdS \tag{3}$$

(2) becomes

$$dU = TdS + \gamma dA + \mu dv \tag{4}$$

where for the system, *)

*) Most of the symbols are borrowed from:

1. KRONIG, R. Leerboek der Natuurkunde, 3de verbeterde druk, Scheltema & Holkema's Boekhandel en Uitgeversmaatschappij N.V., Amsterdam (1951).

2. ZERNIKE, Thermodynamica en Statistiek in de Chemie, 2de druk, N.V. Uitgevers-Maatschappij AE. E. Kluwer, Deventer-Djakarta (1950).

U : internal energy

δQ : a small quantity of heat given to

δW: a small quantity of work done on

μ : energy required to add a unit of substance to the system passing along a quasistatic manner at constant surface area of the interface [12])

ν : quantity of substance in the system

T : absolute temperature

S : entropy

γ : surface tension

A : surface area.

F : free energy, (U-TS), see below

When then the gas phase, is saturated with the liquid vapour, then there exists equilibrium of mass transfer through the liquid-gas interface, e.i. $d\nu = 0$, so equation (4) becomes.

$$(d\mu)_\nu = Tds + \gamma dA \tag{5}$$

The free energy $(F)_\nu$, for ν is constant, which is formulated as

$$(F)_\nu = (U)_\nu - TS \tag{6}$$

gives after differentiation

$$(dF)_\nu = (dU)_\nu - TdS - SdT \tag{7}$$

Substitution of (5) in (7) gives

$$(dF)_\nu = SdT + \gamma dA \tag{8}$$

When the phenomenon occurs isothermally, then

we obtain $\qquad (dF)_{\nu,T} = \gamma dA \tag{9}$

or

$$\gamma = \left(\frac{dF}{dA}\right)_{\nu,T} \tag{10}$$

At constant temperature, a system consisting of a liquid phase and a gas phase, which is saturated with vapour of the liquid, has, if the system has still the two phases in equilibrium, a constant vapour pressure too, hence equation (10) can be written as

$$\gamma = \left(\frac{dF}{dA}\right)_{\nu,T,P} \tag{11}$$

For a liquid having more than one constituent in equilibrium with its vapour mix, equation (11) becomes

$$\gamma = \left(\frac{dT}{dA}\right)_{\nu_1, \nu_2, \nu_3, \ldots, T, P.} \tag{12}$$

Therefore surface tension is defined as a quantity, which is numerically equal to the free energy increase in a system on creating a unit area of new surface at constant composition, temperature and pressure.

c. *Surface tension lowering by addition of soap or its substitute.*

Soaps or their substitutes can reduce the surface tension of water at the gas-liquid interface, thus facilitating the formation of foam in water. The soap acts, then as foaming or frothing agent.

The relation between surface tension and concentration of surface-active agent is usually expressed by the surface concentration equation of Gibbs [13])

$$a = \frac{\alpha}{RT} \frac{d\gamma}{d\alpha} \tag{13}$$

where a = amount of solute per unit area of surface adsorbed or concentrated in the surface or interfacial layer

α = activity of the solute (α = fc for c = concentration and f = activity coefficient)

R = gas constant

T = absolute temperature

γ = surface tension

From the above equation it follows that the adsorption of a dissolved substance is positive when $d\gamma/dc$ is negative, that is when further addition of the solute lowers the surface tension.

Experience has shown that relatively low concentrations of highly surface-active substances lower the surface tension of water to a marked degree, and thereafter the surface tension remaining approximately constant, or even passing through a minimum followed by a shallow maximum but still at a surface tension far below that of the solvent [14]).

d. *Stabilizing of foam.*

A stable foam in water can be formed, when finely divided unsoluble solids pass into the interface of the water and the gas phase and building mechanically strong films. Finely divided clay that may or may not be of colloidal dimension is usually used as foam stabilizer [15]).

Thus in the present experiments, we are dealing with the building of foam of clay, the finely divided portion of which acts as foam stabilizer.

2. Gelling of Clay-Water System.

   a. Kaolin, the basic material for the processing.

   Kaolin is one of the most important varieties of clays, containing as its main constituent the mineral kaolinite, which has the empirical oxide formula $Al_2O_3.2SiO_2.2H_2O$. Kaolinite particles are hexagonal plates with variable thickness and diameter; it has been reported that most of the particles are 50mμ in diameter and 10mμ thick [16]).

   Clays may be considered to be formed by natural hydrolysis of feldspar, a potassium aluminosilicate, and various alkaline aluminosilicates, by atmospheric action [17]);

   $$K_2O.Al_2O_3.6SiO_2 + 2H_2O + CO_2 \rightarrow$$
   $$Al_2O_3.2SiO_2.2H_2O + 4SiO_2 + K_2CO_3 \qquad (I)$$
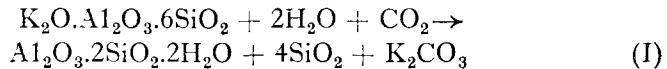
   The combined water of clays present as hydroxyl group as denoted by the formule $Al_2(OH)4(Si_2O_2)$[16]), which corresponds to the atomic arrangement after HAUSER [18]) as shown in Figure 1.

   According to reaction (I), normal clays always contain besides undecomposed feldspar and silica, more or less metals, particularly alkalies and alkaline earths. A substitution of the trivalent for the tetravalent silicon leaves one negative charge upon the lattice which has to be compensated by free positive ions upon or near its surface [19]). No doubt, ions of the above alkalies and alkaline earths are bonded by the negative clay forming the so called salts of clay.

   Tropical soils in rainy regions have much of the metals washed out by water, leaving the acid or hydrogen clay [20])

   b. Electric charge on clay particles.

   Under neutral or alkaline conditions, by ionization of the salts of clay or hydrogen clays, the clay particles become thus negatively charged. That this is the case was first performed by REUSS [21]) in 1808 by treating a clay hydrosol to electrolysis,

which showed that the clay particles moved to the positive electrode, a phonomenon that is usually called cataphoresis or electrophoresis.

According to FORD, LOOMIS and FIDIAM [22]) broken edges on clay particles exposing aluminum ions will be positive,
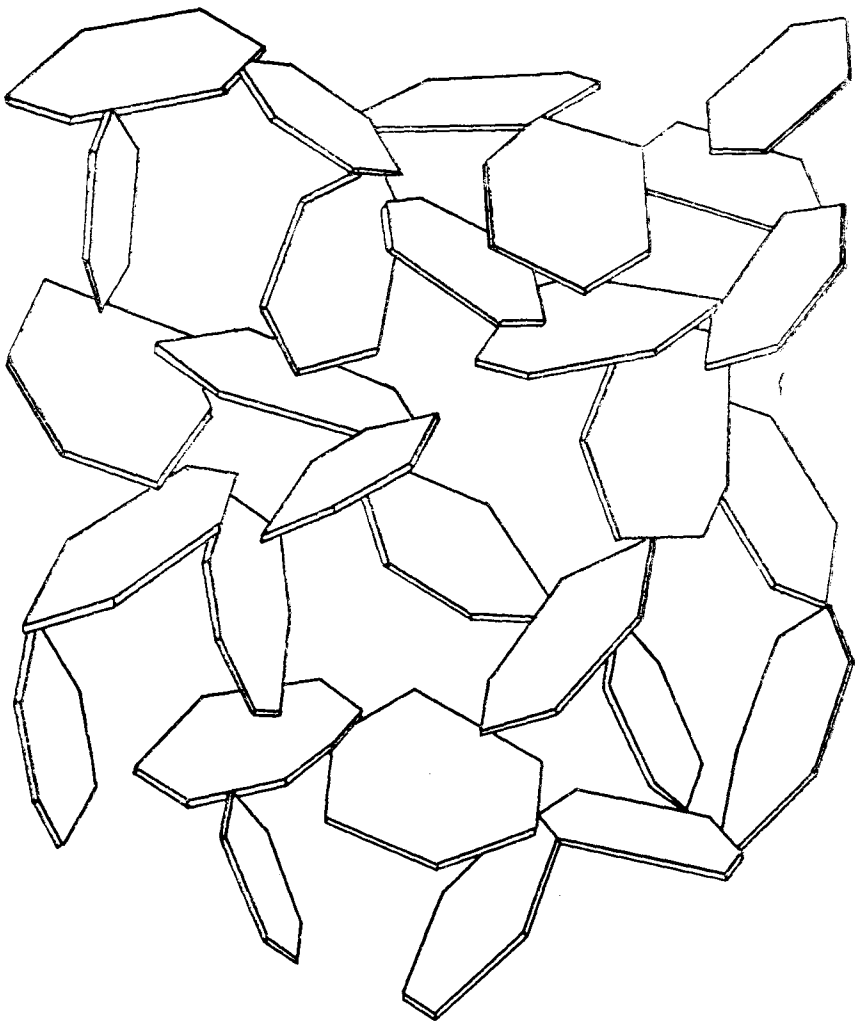
Figure 1
Atomic arrangement in kaolinite after HAUSER [18]).

whereas the other edges will be negative. Direct evidence for
positive edge sites kaolinite was found earlier by THIESSEN [23]
and later by MERING and his coworkers [24] who obtained electron
micrographs showing very clearly the attachment of negative
gold sols at the edges of the clay flakes.

c. Flocculation and gelling of clay particles in water.

In a salt free system and slightly acid conditions, positive
charges can develop on the edges of the clay plates giving rise
to an edge-to-face type flocculation, because of the existence
of electrostatic attraction between positive edge and negative
face of the clay particles [25]. Such a flocculated system is often
described as resembling a house of cards [25,26] as is shown in
Figure 2. [26]

$\odot$ = OH $\bigcirc$ = O

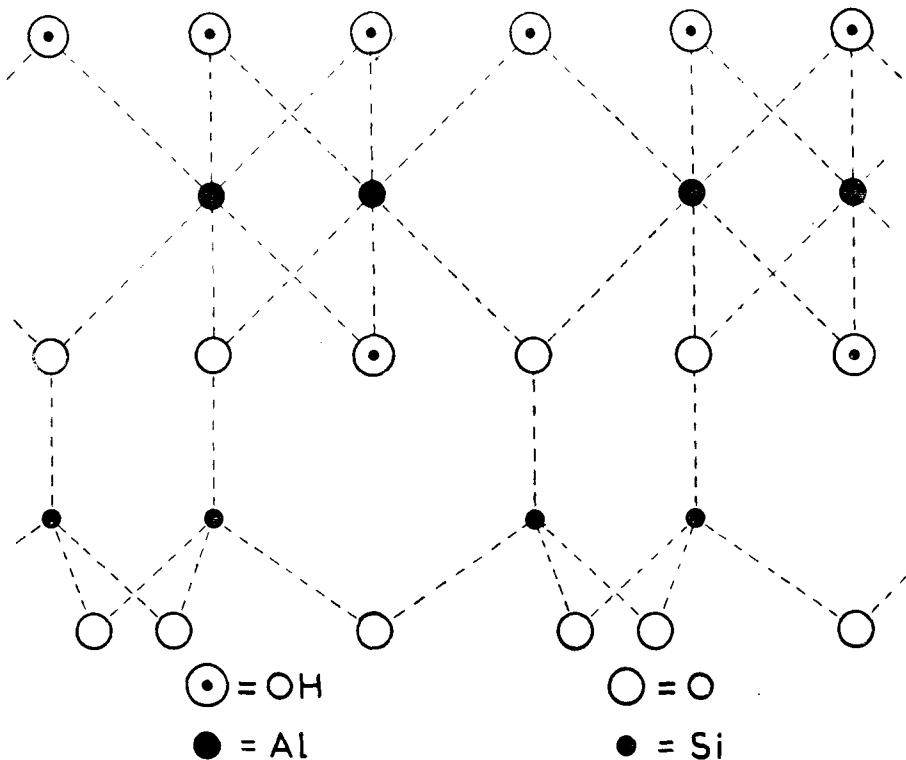$\bullet$ = Al $\bullet$ = Si

Figure 2.
House of cards flocculated system of kaolinite particles [26].

When the clay suspension is dense enough, a firm gel can be built-up.

By addition of small amounts of electrolyte, clay suspension which exhibits little or no gelling tendency can be converted into a gel [27]).

Because there is no sharp limit between gel formation and the formation of flocculatous precipitates [28]), in the present investigation the author used sodium fluosilicate as gelling agent, which has a delayed gelling action, and which is commonly used in the rubber industry for the preparation of foam rubber from latex.

d. The terms gel and xerogel.

HERMANS [29]) assigns the term gel to a system characterized by the following points:

i)   there are coherent colloid disperse systems of at least two components;

ii)   they exhibit mechanical properties characteristic of the solid state;

iii)   both the dispersed compenent and the dispersion medium extent themselves continuously throughout the whole system.

In case of gelled clay system, after evaporation of the water, a harder and a stronger system which is called xerogel is formed. The evaporation process is accompanied by a shrinkage corresponding approximately to the volume of liquid removed [30]).

e. Sodium fluosilicate, the gelling agent.

As said in c. in the present experiments sodiumflu osilicate is used for the gelling of clay system. The rather high acidity of the salt in water and its low solubility, viz. 0,76 grams in 100 grams of water at 25°C. [31]), makes it most suitable, thus prevents overdosage and local high concentration of acid formed to hydrolysis, which after KUBELKA and PRISOUPIL goes as follows [31]):

$$2H_2O + SiF_6^= \rightarrow 4H^+ \; 6F^- + SiO_2 \qquad (II)$$
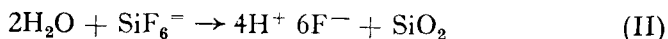
Sodium fluosilicate was used since 1925 as coagulant for rubber latex by STEVENS [32]) and for the first time as gelling agent for the manufacture of foam rubber in 1929 by the DUNLOP RUBBER Co., Ltd. [33]).

In the presence of sodium fluosilicate the pH of the clay slip decreases, hydrogen ions adsorbed on the clay particle, so the effective negative charge on the particles diminishes, thus facilitating the approaching to each other of individual particles followed by the formation of a gel.

III. Preparation of green foam brick.

1. Mixing the Ingredients.

Kaolin from the island Bangka, commonly called Bangka clay, was used for the experiments. Lumps (composed of sticked fine powder) of the mineral were crushed in a mortar, and dried for at least five hours in a drying oven at 110°C.

The cooled crushed clay was then grinded in a hammer mill, and afterwards screened. The portion smaller than the mesh number 80 of the U.S. Sieve Series, which corresponds to 0.177 mm. [34]), was used as the starting material for the foam clay ware.

The mixture used by the author for preparing the foam product in laboratory scale had the following composition (in grams).

Kaolin, Bangka clay, 80 mesh	700
"Teepol" solution, 22% freshly prepared from a 40% solution	390
Bentonite powder	4.2
Sodium fluosilicate, technical grade	11.2

The above compounded mix was used for the preparation of two samples, which were cast in two same moulds having the dimension of 20 cm. in length, 7 cm. in width, and 5 cm. in height, made of galvanized iron sheet.

The liquid part of the ingredient for the mixture was prepared by making a bentonite suspension of 15% in the "Teepol" solution first, followed by addition of the sodium fluosilicate to

the bentonite slip until a proper dispersion was formed. Here the bentonite was used as dispersing agent for the practically insoluble sodium fluosilicate in water. The mixing procedure was as follows, To 24 g. 2.2% "Teepol" solution, which was placed in a mortar was added 4.2 g. bentonite slowly. The mixture was then homogenized by grinding with a pastile and finally the 11.2 g. of the sodium fluosilicate added there in, under thouroughly grinding. About a third portion of the bulk surfactant solution was then poured little by little in the mortar, the viscous slip formed was transfered to a beaker, while the rest or the solution was used for rinsing the mortar. The whole amount of the dispersion was then prepared to be used for the process.

The dispersion was afterwards added to the 700 g. kaolin portion by portion which was placed in a pan, under, thouroughly kneeding and stirring by means of a spatula. By such treatment one should obtain a clay slip having a consistency like that of ice cream. This mixing period lasted about 5 minutes.

The mixture was then beated. For the experiments the author used a common egg beater consisting a curled iron wire as the beating part, which is attached on the top of a wooden handle.

After 10 minutes beating with a beating intensity of three strikes per second, the foamed slip was transfered by means of a trowel to the two moulds.

The following paragraph would elucidate the casting procedure done by the author.

2. Casting the Foamed Slip.

Before being used, the inner walls of the mould were wetted with the "Teepol" solution and afterwards coated with sawdust having a grain size smaller than the mesh number 60 of the U.S. Sieve Series, which corresponds to 0.250 mm. [32] Such treatment would make the releasing of the cast ware from the mould easier, and the more because in the presence of the saw-dust layer, creeping of the clay ware due to shrinkage during the evaporation process of the water, can run very smoothly. The air chick proceeds between the clay ware and the wall of the mould, after the system

has been allowed to stay during the drying period, facilititates the evaporation process too.

The foamed clay body can be released 3 days after it was cast.

3. Drying the Clay Gelled Foam.

The releasing of the foam product was done as follows. A wooden plank having the dimension conformable to the open side of the mould was placed on the mould opening, followed by turning the system upside down and at last lifting the mould carefully leaving the green ware lain face down in the plank.

The product was then dried at room temperature during one week or more.

IV. Conclusions.

1. "Teepol" proves to be useful for the foaming prosess of clay slip.

2. A firm clay gel can be produced by using sodium fluosilicate as gelling agent.

3. Coating of the inner walls of the mould with saw-dust makes the releasing of the cast clay ware from mould easier.

4. Physical data of the foam brick will be reported in Part II of this investigation.

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