A STUDY ON THE WASHING OF MILK OF MAGNESIA THROUGH A PERMEABLE MEMBRANE.*

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Milk of Magnesia is usually prepared by precipitating magnesium hydroxide from a solution of magnesium sulphate by means of sodium hydroxide. The sodium sulphate resulting from this double decomposition, along with any excess sodium hydroxide must be removed from the magma, or suspension of hydrated magnesium hydroxide. This removal of electrolytic impurities from the milk of magnesia, technically called "washing" the milk of magnesia, is usually not carried out by filtration methods in view of the adverse effect upon the stability of the suspension which seems to accompany any thickening of the milk of magnesia to the extent necessary in that procedure.[2] The degree of thickening which occurs during the settling of the suspension in decantation methods of washing does not seem to be detrimental to the subsequent stability of the product, and decantation methods in some form or another are therefore in fairly general use.

The decantation method involves, however, some very important disadvantages. The rate of settling is very slow even when the temperature is maintained well above that of the room in order to hasten it. Due to this required temperature maintenance and to the long periods of time required for settling between each decantation, the method does not lend itself to the economy in water that could accrue through using, in the earlier stages of the washing of any particular batch, water which has already been used for the later stages of the washing of previous batches.

Without considering, for the moment, any technical questions of handling in plant practice, it seemed that these difficulties could be obviated in a method whereby the milk of magnesia is washed by means of wash water separated from it by a permeable membrane. It was to be expected that the diffusion of electrolyte through that membrane would require much less time than that required by the repeated settlings.

In taking up a theoretical consideration of the problem of washing milk of magnesia by means of the diffusion of the electrolyte through a permeable membrane into the wash water on the opposite side of that membrane, it will be seen that Fick's Law will require some alteration.

Thus, Fick's Law states that the amount of solute d S which will cross a given cross-sectional area "a" in time dt, is expressed by

$$\frac{dS}{dt} = -Da\frac{\delta_c}{\delta x}$$

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[2] We have at present no experimental basis for a theoretical discussion of the factors which determine the stability, or other physical characteristics of the milk of magnesia. Based upon general theory and analogy with colloidal hydrous oxides which have been more closely studied, we have assumed the colloidal character of milk of magnesia to be $[MgO].(H_2O)x$ and that any mechanism which will bring about a decrease in the value of x will cause the stability of the suspension to be decreased.

when $\frac{\delta_c}{\delta^x}$ is the concentration gradient in the direction of x, and when D is the so-called diffusion constant or specific diffusion rate for the solute in question.

Under the conditions of our proposed experiment there will be the additional circumstance that free diffusion of the solute will be impeded by the permeable membrane. This impedance factor would be a constant, characteristic of the chemical nature, physical texture and thickness of the membrane. Therefore the value of D would be altered by the constant factor K.

$$\frac{dS}{dt} = -K\,Da\,\frac{\delta_c}{\delta x}$$

If we should now accept the additional condition that the milk of magnesia on the one side of the permeable membrane and the wash water on the other side of that membrane shall be agitated so that no concentration gradients of electrolyte shall exist on either side of the membrane, then the concentration gradient $\frac{\delta_c}{\delta^x}$ can be replaced by the factor $(C^M - C^W)$ in which C^M is the concentration of electrolyte in the milk of magnesia and C^W is the concentration of electrolyte in the wash water, so that the question of distance is eliminated except in so far as it implies the two sides of the membrane. Thus,

$$\frac{dS}{dt} = -K\,Da\,(C^M - C^W)$$

One more condition of the proposed experiment differs from simple diffusion, namely, that some solute will be adsorbed on the extensive surface of the milk of magnesia. This factor will be important in so far as it affects the value of $(C^M - C^W)$ in the above formula. This value can of course be affected by this adsorption only by affecting the element C^M. Since only the non-adsorbed part of solute in the milk of magnesia is freely diffusible, C^M refers only to the non-adsorbed portion of the solute in the milk of magnesia. The total concentration of solute within the milk of magnesia is equal to

$$C^{M\ \text{total}} = C^{M\ \text{adsorbed}} + C^{M\ \text{free}}$$
$$\text{or}\quad C^{M\ \text{free}} = C^{M\ \text{total}} - C^{M\ \text{adsorbed}}$$

but from the well-known Freundlich adsorption isotherm we can see that

$$C^{M\ \text{free}} = C^{M\ \text{total}} - MK\,C^{M\ \text{free}\ 1/n}$$

M = quantity of adsorbent
K and n = constants characteristic of adsorbent and substance adsorbed.

Due to the configuration of the exponential curve for the value $-MK\,C^{1/n}$ (the Freundlich adsorption isotherm) we know that for large values of $C^{M\ \text{free}}$ the *relative* values of the adsorbed material are small so that $\frac{C^{M\ \text{free}}}{C^{M\ \text{total}}}$ = almost unity, and the error due to dropping the adsorbed solute from consideration is small. When the value of $C^{M\ \text{free}}$ becomes small then *relatively* the importance of the adsorbed solute becomes enormously larger, due again to the configuration of the exponential curve for $-MK\,C^{M\ \text{free}\ 1/n}$ (Freundlich adsorption isotherm). Now, the value of $\frac{C^{M\ \text{free}}}{C^{M\ \text{total}}}$ can become much less than unity.

At any rate, the theoretical basis upon which the problem should be viewed is the following equation which has been derived in the above manner from Fick's Law of Diffusion and Freundlich's adsorption isotherm.

$$\frac{dS}{dt} = -K\,Da\,(C^{M\ \text{total}} - M\,K\,C^{M\ \text{free}\ 1/n} - C^W)$$

In practice, the importance of segregating for special consideration this influence of adsorption will depend upon the efficiency of the suspended material as an adsorbent and the capillary activity of the solute. If one were to attempt, for example, to wash an efficient adsorbent material like a suspension of kaoline free from a highly capillary active solute like butyric acid the phenomenon of adsorption might become the factor of utmost importance and the simple diffusion of the unadsorbed portion the factor of lesser importance.

In the specific problem with which we were confronted the solute which was mainly sodium sulphate was a substance of very low capillary activity; the suspended semi-colloidal hydrated magnesium hydroxide was, however, a fairly efficient adsorbent. That adsorption phenomena play a rôle in the progress of the "washing" of milk of magnesia was not doubted. Since preliminary experiments by the diffusion method and past experience with the decantation method gave no indication that this phenomenon was sufficiently influential to present any special problem, no effort was made to determine its magnitude experimentally. The experimental work to be described was not carried out for the purpose of obtaining data with which to test the validity of the above equation or to obtain numerical values for the various factors involved. The work was entirely preliminary in nature, and its sole purpose was to gain some conceptions as to the type and size of equipment which might be required to "wash" milk of magnesia by a diffusion method, as well as the economies in time and water that might be inherent in such a method.

In spite of the fact that the equation derived was not actually used with the data presented in this paper, the mathematical analysis upon which it is based did furnish the complete understanding of the factors involved in this method of washing milk of magnesia which was deemed necessary to the proper planning of the experimental work.

EXPERIMENTAL.

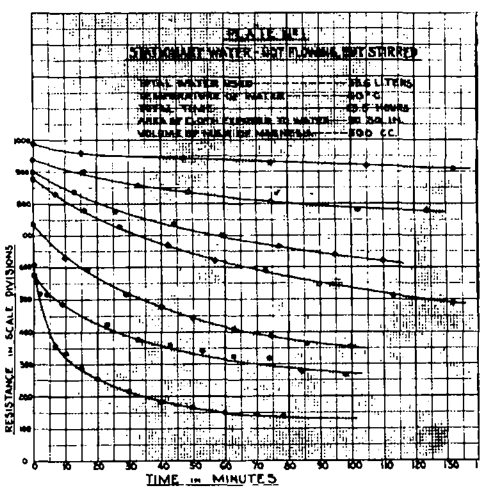
A cylindrical bag made of canvas filter cloth, three inches in diameter and eight inches high, was suspended in the center of a two-gallon crock, so that the bottom of the bag remained about one inch from the bottom of the crock. A 500-cc. sample of recently precipitated milk of magnesia was put into the bag and enough water into the two-gallon crock to bring it to the same level as that of the milk of magnesia. This required 4800 cc. of water. Both the milk of magnesia within the canvas bag and the water outside this bag were continually and vigorously agitated by means of motor-driven stirrers in order to fulfil the requirement that no concentration gradient of electrolyte should exist either in the milk of magnesia or in the water, and also so that the milk of magnesia should not be able to settle nor to form crustations upon the inner surface of the bag. The progress of the diffusion, or "washing," was followed by means of periodic conductivity measurements on the wash water. No effort was made to record these conductivity measurements in absolute units. In fact, they were recorded in arbitrary scale readings which were equal to the reciprocals of the conductivities multiplied by a constant; *i. e.*, ohms $\times$ constant. A resistance of about 900 scale divisions was from previous work known to be that which corresponded to a fully "washed" milk of magnesia; the same conductivity cell being used throughout. Distilled water so measured gave a reading of 1000 scale units.

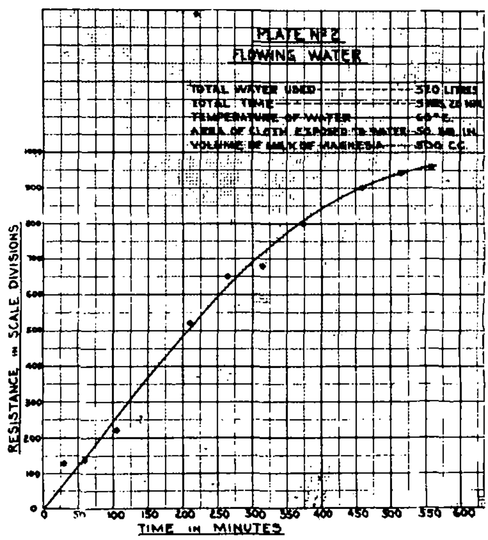
As equilibrium between the concentrations of the electrolyte in the milk of magnesia and in the wash water is approached, the time-resistance curve tends to become parallel to the line of abscissæ. When this tendency made itself apparent the particular portion of wash water was considered spent and was replaced by another portion. Plate No. 1 shows these time-resistance curves for each portion of wash water.

In order to wash the 500-cc. sample of milk of magnesia to a conductivity of 1/910 scale divisions a total of 33.6 liters of water was required, and an elapsed time of 13.5 hours at 60° C. This is five times as much water as was used in a parallel washing of the same quantity of milk of magnesia by the decantation method, but the result was accomplished in only one-tenth of the time required by the decantation method.

The relatively larger quantities of wash water used in this method than those used in the decantation method are not inherently required by the diffusion method; but result from the use of rather large portions of wash water. As is well known, great economy of wash water for the washing of precipitates can be effected by the use of many small portions of wash water rather than a few large portions. For the same mathematical reasons, similar economy can be brought about in the diffusion method of washing by the use of many and smaller portions of wash water outside the bag.

In order to investigate the economy of water to be effected by the use of very small portions of water each brought fairly close to equilibrium with the milk of magnesia, before discarding it, it was considered expedient to abandon the use of mechanical agitation of the several portions of wash water and to allow it to flow through an annular space between the canvas bag holding the milk and the external vessel. This was accomplished by the simple procedure of substituting a smaller





vessel around the canvas bag described in the above experiment, so that the walls of the vessels were about one inch distant from the walls of the bag. The water was allowed to flow in at the bottom and to overflow at the top. The annular space was, of course, still too large to allow the linear rate of flow of the water to be sufficiently rapid to provide good agitation and at the same time to be in contact with the canvas bag for a sufficiently long time to come into equilibrium with the milk of magnesia.

It would, however, have presented too many mechanical difficulties to provide an annular space so small that the linear flow could have been rapid enough to be turbulent and still allow the required length of contact. In the absence of these mechanical requirements either time or water economy had to be sacrificed, and it was decided for the moment to sacrifice the latter. It will be seen from the graphical representation of the result in Plate No. 2 that the time required to accomplish the complete washing of the milk of magnesia was still further reduced, indicating that when the annular space occupied by the wash water is sufficiently small, it is not necessary in practice to provide mechanical agitation to the wash water providing it is flowing at a moderate rate. From a consideration of the data on Plate No. 2 it will be seen also that due to the balance struck between the various factors it was not possible with equipment of the dimensions used to retain the full advantages of water economy without making a compensatory sacrifice of time.

It would be theoretically possible, of course, to adjust the dimensions of the equipment so that fuller advantage of the economies in both time and water could be had. Practically, however, this would be difficult and it was decided to pass immediately to the more practical experiment about to be described.

As intimated in the introduction, the saving of time afforded by the diffusion method of washing milk of magnesia makes it possible to consider a counter-current system. Such a system, if designed for continuous operation, would require long canvas tubes through which the milk would have to pass very rapidly in order to obviate deposition of magnesium hydroxide on the canvas walls. The mechanical difficulties involved in such a method would be considerable, and since we were concerned only with evaluation of the principle, an intermittent counter-current system was employed.

Each of five canvas bags was charged with 400 cc. of milk of magnesia, and suspended in a separate washing vessel containing three liters of wash water. Crude milk from the precipitation kettle met, in the first washing unit, wash water high in sodium sulphate (its washing power almost spent), and was allowed to remain therein until the curve, constructed for time against resistance approached a horizontal straight line, indicating that concentration of solute in the wash water was nearing the concentration of that in the milk. The bag was then removed to the second washing unit where the initial concentration of sulphate in the wash water was lower. Finally the fifth wash was distilled water, in which the bag was left until the milk showed a conductivity of 1/900 scale units.

Regular operation of this discontinuous counter-current system showed that one charge was completed every two and one-half hours. A complete washing, therefore, required twelve and one-half hours, and while actually coming in contact with fifteen liters of wash water, each charge required only three liters of fresh water.

The economy of water obtained in this manner was, of course, very great. The amount of water used was only one-half of that required by the decantation method for an equivalent volume of milk, and only one-tenth of the amount required by the diffusion method in the first experiment above described.

The question of any practical utilization of this scheme would depend on a great many points, the consideration of which was not undertaken. It was possible from the above results, however, to calculate the dimensions which would be necessary for washing any given quantity of milk of magnesia in such a system.

Mathematically it is apparent that any of the dimensions of the canvas bags containing the milk of magnesia can be altered at will, so long as the amount of water which was found necessary to wash a given volume of milk is supplied and so long as the following relationship is maintained.

$$\frac{\text{Area of interface} \times \text{Time of exposure}}{\text{Volume of milk}} = \text{Constant}$$

Substituting the values found in the laboratory experiment, in which five bags, each containing 400 cc. of milk of magnesia, were washed 12.5 hours:

$$\frac{191.4 \text{ sq. in.} \times 12.5 \text{ hours}}{0.529 \text{ gal.}} = 4522 \text{ sq. in.-hours per gal. of milk}$$

Applying this data to plant scale equipment, a series of five canvas bags three feet in diameter by four feet high, having a total capacity of 1060 gallons of milk and a total effective area of 32,290 square inches would require 148 hours for complete washing, thus delivering 172 gallons of finished milk per 24 hours. Six such operating units would deliver approximately 1000 gallons.

These calculations are of course correct only in proportion to the extent to which the fundamental factors can be maintained unchanged in passing from a small laboratory scale to the plant scale. That this cannot be done is best illustrated by the fact that in the system we have visualized for plant practice, each outer vessel must contain 1590 gallons of wash water. Therefore it must be eight feet in diameter, if the bottom of the bag is to be one foot from the bottom of this kettle. Since the cloth bag containing the milk of magnesia is only three feet in diameter the annular space between the containers will be two and one-half feet. This is hardly comparable to the one-inch annular space in the laboratory equipment. The abandonment of agitation in the external wash water in the laboratory experiment was based on the rapid diffusion of the sodium sulphate and the small annular space, *viz.*, one inch, so that the concentration gradient could still be considered negligible. This would hardly hold good in the plant-size equipment now visualized and therefore one would need to assume agitation on both sides of the canvas once more in order to use these calculated dimensions.

SUMMARY.

A mathematical analysis has been presented for the case of washing a material in suspension by means of water separated from it by a permeable membrane. The effect of adsorption as well as simple diffusion has been considered, and an equation derived from Fick's Diffusion Law and Freundlich's adsorption isotherm.

A practical evaluation of this method of washing as applied to milk of magnesia has been carried out.

PHYSICIAN AND PHARMACIST.*

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The past quarter of a century has witnessed rapid changes in the character of the retail drug business. However, the drug store is and always has been an essential and responsible factor in caring for public health. To what extent this position will be preserved depends, I believe, somewhat upon what we as pharmacists do in our position in a triangle involving physician—yes, dentist and nurse, and pharmacist and the public.

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