

## LETTERS TO THE EDITOR

From the editors

Following the publication of a letter by V. G. Levich "Concerning One Sensational Effect" (Usp. Fiz. Nauk 88, 787 (1966) [Sov. Phys. Uspekhi 9, 316 (1966)] concerning the influence of the magnetic field on the properties of water, the editors received several letters expressing a wide range of opinions. In some letters it is indicated that the question has a technical significance and that it is necessary to explain the influence of the field on the water; these authors back V. I. Klassen firmly. In other letters, the authors support the point of view of V. G. Levich with respect to water in homogeneous solutions, and simultaneously indicate that the field can influence the impurities in the water, and then indirectly, via the impurities, the crystallization of aqueous solutions. In this aspect, the existence of the effect does not contradict the general principles of physics defended by V. G. Levich; at the same time, if the impurities play the principal role, then the problem is one of colloid chemistry and should not be published in this journal.

We present below a letter by O. I. Martynova, B. T. Gusev, and E. A. Leont'ev, which in the editors' opinion contains the most convincing and direct experimental data. In publishing this letter, the editors terminate the discussion on the pages of this journal.

*CONCERNING THE MECHANISM OF THE INFLUENCE OF A MAGNETIC  
FIELD OF AQUEOUS SOLUTIONS OF SALTS*

O. I. MARTYNOVA, B. T. GUSEV, E. A. LEONT'EV

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COMMUNICATIONS devoted to the influence of an external magnetic field and various technological processes occurring in an aqueous medium, have appeared recently not only in the popular but also in the technical literature, and still continue to appear. Most communications are characterized primarily by a very free treatment of the concept of "water," which frequently borders on a misunderstanding of the fact that there is a great difference between the substance corresponding to the formula  $H_2O$ , on the one hand, and tap water, river water, and even distilled water on the other.

Failure to take into account the nature of various types of technological water accounts apparently for the unusually unstable and quite frequently contradictory results obtained in the field where "magnetic treatment" of water with the aid of so-called "magnetic apparatus" of various designs has received perhaps its greatest use, namely on the field of prevention of scaling in low-pressure steam boilers. Magnetic treatment of water, regardless of the design of the apparatus, always involves the passage of the water, prior to its entry into the heat exchanger, through "magnetic apparatus" in which the field has an intensity of several thousand Oersteds.

According to carefully verified data, both experimental and commercial, such treatment of water containing hardness-producing salts indeed leads in many cases to a decrease in the amount of hardness salt (scale) that crystallizes during the boiling of the water on the heated surfaces, and increases the amount of salts that crystallize in the volume (the so-called sludge). But in other cases, treatment under the same conditions and in the same apparatus produces no effect whatsoever.

Such exceedingly contradictory results can be con-

nected only with a complete failure to take into account a very important factor—the compositions of the various types of water.

In this connection, certain investigations were undertaken in the Water-technology Department of the Moscow Power Engineering Institute (MEI) for the purpose of determining the influence of the composition of the water—as a rule, a complex solution of various components—on the changes occurring in a number of the characteristics of the water, and particularly on the characteristics called in industry the "antiscaling effect" following magnetic treatment of the water. It is usually defined as the difference (absolute or relative) between the amount of scale produced on the walls of the heat exchanger by water previously untreated or treated with a magnetic field.

In the experiments, the following were made to flow at low velocities (0.1 m/sec) through a magnetic field of intensity up to 9000 Oe: a) technological water of varying composition, b) artificially prepared solutions of certain hardness-causing salts ( $CaSO_4$ ,  $CaSiO_3$ ,  $BaSO_4$ ,  $Ca(HCO_3)_2$ ) in distilled water, and c) water corresponding most closely to the composition  $H_2O$ , prepared from water first desalted with an ionite filter and then triply distilled under special conditions. The field direction was perpendicular to the liquid flow. Some of the experiments were performed also under static conditions. The time of action of the magnetic field on the water in the kinetic experiments amounted to 2 sec, and in the static experiments to 35 min. The chemical composition of the solutions and the aforementioned antiscaling effect were monitored by letting technological water (solutions) flow directly from the magnetic apparatus into the tube of the heat exchanger. Certain phys-

ical characteristics (electrical conductivity, optical density, refractive index, and also electron-microscope photographs) of technological water and hardness-salt solutions, as well as of pure  $H_2O$ , which were readily measured, were also monitored before and after application of a magnetic field.

The investigations have established, first, that the monitored physical characteristics (electrical conductivity and optical properties) of pure  $H_2O$  do not change in the least under the influence of a magnetic field. An electron-microscopic investigation (using an EM-5 microscope) of pure  $H_2O$ , performed by instantaneous freezing of drops of selected samples on a copper block cooled by liquid nitrogen and obtaining single-step carbon replicas, has shown a smooth amorphous surface without any crystalline inclusions; if any ice crystals were present following the employed procedure of instantaneous freezing, their dimension did not exceed  $50 \text{ \AA}$ , as determined by the resolving power of the microscope.

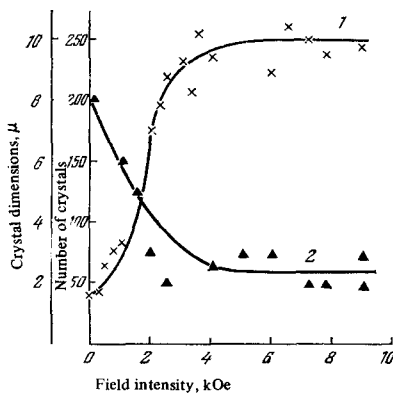


FIG. 1. Influence of magnetic field on the precipitation of the solid phase of calcium carbonate (calcite) from a supersaturated solution of calcium bicarbonate. 1 - Number of crystals; 2 - crystal dimension.

At the same time, some of the investigated types of technological water and hardness-causing salt solutions revealed changes in the aforementioned physical characteristics under the influence of magnetic treatment, as well as greatly differing electron-microscope carbon replicas. This was a result of crystallization, within the volume of the solution, of a certain amount of hardness salts; special experiments have demonstrated that the dimensions of the produced crystals decrease (and accordingly their number increases) with increasing magnetic field intensity (Fig. 1).

As a result of the investigations, we can formulate the following main conclusions.

The feasibility, in principle, of an influence of a magnetic field on the decreased rate of scaling on the walls of heat-exchange apparatus is determined by two factors that are connected with the properties of the treated water (solution):

a) The first factor is the thermodynamic non-equilibrium state of the solution, i.e., its supersaturation with hardness salts at the instant when the magnetic field acts on the solution. In this case there occurs in the volume a rapid crystallization of the excess amount of

hardness salts; the process continues until equilibrium is established under given concrete conditions, i.e., until saturation concentration is reached, the magnitude of which is not altered in any way by the action of the magnetic field.

The precipitation from the supersaturated solution of a relatively small (compared with the total salt content) amount of crystals, for example calcium sulfate or calcium carbonate, does not change to any degree the total amount of the solid phase released during the subsequent evaporation of the solution. However, the small crystallites that are produced by magnetic treatment of the water prior to its entry into the heat exchanger (steam generator) act as so-called "primers," i.e., crystallization centers, in the heat exchanger. If the number of such centers is sufficiently large, further crystallization of the salts following extensive evaporation of the water in the steam generator, occurs to a considerable degree on these centers, and not on the heating surfaces, i.e., the rate of scale formation decreases.

If the solution is not supersaturated at the instant when it passes through the magnetic field, no "primer" crystals are produced, and upon further evaporation of the solution (water) in the heat-exchange apparatus the hardness-salts are crystallized in the form of scales on the heating surface.

b) A second factor is the inevitable presence in the magnetically-treated water of iron oxides (or of some of their hydrate forms). They are always present in any technological water or simply distilled water (obtained, e.g., by single distillation in the laboratory distiller D-1, type 734); under practical conditions, it is a very complicated matter to obtain water completely free of iron oxides, or at least with a concentration of such oxides lower than  $0.001 \text{ mg/kg}$ .

The iron impurities in various types of technological water, and also in distilled water, are the predominant corrosion products of different parts of the apparatus; a number of these products, such as  $Fe_3O_4$  (magnetite),  $\delta-FeOOH$ , and  $\gamma-Fe_2O_3$  have ferromagnetic properties. The form in which such partially hydrated oxides exist is mainly colloidal, since their true solubility is very low, and as a rule is lower than the iron concentrations characteristic of most water used in power engineering ( $10^{-6}$ – $10^{-4}$  mole/kg); on the other hand, ionic forms cannot be stable, since they are subjected to deep hydrolysis, this being contributed to by the low values of the dissociation constants of the corresponding hydrate forms, especially at increased temperatures.

In the experiments performed at MEI they investigated, in particular, the influence of the magnetic field on supersaturated solutions (supersaturation coefficient 1.04) of calcium sulfate, prepared a) with ordinary distilled water (iron concentration  $0.13$ – $0.20 \text{ mg/kg}$ ) and b) specially prepared triple distillate, in which the presence of iron could not be established (the sensitivity of the method was  $(0.001$ – $0.003) \text{ mg/kg}$ ). A simple visual observation, as well as examination in an electron microscope of replicas of samples of supersaturated calcium-sulfate solutions, not treated by a magnetic field, have shown a relatively smooth relief of the surface with a slight amount of crystalline inclusions (Fig. 2). At the same time, samples of a solution of calcium sulfate pre-

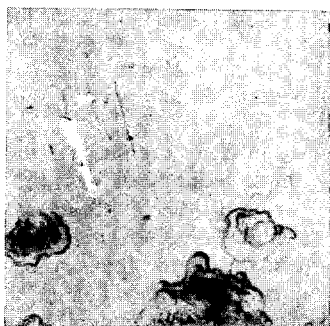


FIG. 2. Carbon replica from contact surface of a frozen drop of supersaturated  $\text{CaSO}_4$  solution not subjected to the action of a magnetic field (20,000X).

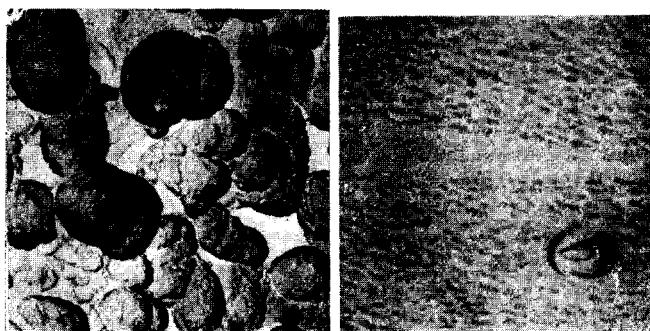


FIG. 3

FIG. 4

FIG. 3. Carbon replica from the contact surface of a frozen drop of supersaturated solution of  $\text{CaSO}_4$  prepared with monodistillate, following the action of a magnetic field  $H = 6000$  Oe (10,000X).

FIG. 4. Carbon replica from the contact surface of a frozen drop of supersaturated solution of  $\text{CaSO}_4$  prepared with tridistillate, following the action of a magnetic field  $H = 6000$  Oe (20,000X).

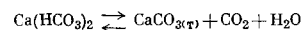
pared with the monodistillate, reveal a clearly pronounced crystal structure after the magnetic treatment (Fig. 3)\*; the crystal structure of a solution of calcium sulfate prepared with the tridistillate, which was practically free of iron, was pronounced to a very small degree (Fig. 4). Corresponding changes occurred also in the electric conductivity and in the optical properties of the investigated solutions, namely, the non-supersaturated solutions, as well as the supersaturated calcium-sulfate solution prepared with the tridistillate, revealed practically no changes after application of the magnetic field, whereas the supersaturated calcium-sulfate solution prepared with the monodistillate revealed an increased optical density after magnetic treatment.

The following can be stated with respect to the foregoing regularities. The waters most abundant in nature, of the so-called bicarbonate class, as well as solutions containing calcium bicarbonate, are quite complicated systems; the ability of precipitating the solid phase of the typical scale, namely of the low-solubility calcium carbonate, is determined by the state of their carbonate equilibrium. Since the feasibility in principle of the ac-

\*The magnetic field has no influence on the crystalline modification of the solid state of the salts.

tion of a magnetic field on such systems is determined primarily by the presence of supersaturation (which, as a rule, was not taken into account in their magnetic treatment), we shall consider briefly the main premises of the conditions for non-equilibrium of solutions of bicarbonates (waters of the bicarbonate class).

The process of conversion of a highly soluble calcium bicarbonate into the low-solubility carbonate



is characterized, as is well known, by a definite relation between the equilibrium concentrations of the dissolved carbon dioxide and of the remaining components of the system:

$$C_{\text{CO}_2}^{\text{eq}} = \frac{K_{\text{II}}}{K_{\text{I}} \Pi P_{\text{CaCO}_3}} C_{\text{Ca}^{2+}} C_{\text{Ca}^{2+}} C_{\text{HCO}_3^-}^2 C_{\text{HCO}_3^-}^2$$

where  $K_{\text{I}}$  and  $K_{\text{II}}$  are the dissociation constants of the carbon dioxide, and  $\Pi P_{\text{CaCO}_3}$  is the product of the solubility of the calcium carbonate. The concentration of the carbon dioxide dissolved in water when the water comes in contact with the gas phase is in turn a function of the partial pressure of the  $\text{CO}_2$ . Under the condition

$C_{\text{CO}_2}^{\text{sol}} < C_{\text{CO}_2}^{\text{eq}}$  the solution is supersaturated and the

solid phase of the calcium carbonate may in principle be precipitated; the process of crystallization can in this case be intensified by the influence of the magnetic

field. If  $C_{\text{CO}_2}^{\text{sol}} > C_{\text{CO}_2}^{\text{eq}}$ , the solution is unsaturated, the

formation of the solid phase of the calcium carbonate is in principle impossible, and naturally, the magnetic field cannot exert any influence whatever.

It is clear from the foregoing that solutions of calcium bicarbonate (water of the bicarbonate class) can, following relatively small changes of a number of parameters (e.g., the temperature or the partial pressure of the  $\text{CO}_2$  over the solution), easily change over from the unsaturated to the supersaturated state. Failure to take this circumstance into account may lead to incorrect conclusions concerning the conditions under which the "magnetic treatment" of such water can be effective.

All the experiments performed on unstable technological water or supersaturated solutions of hardness salts prepared with water containing iron oxides have shown that their passage through a magnetic field leads, following subsequent evaporation of the water in heat-exchange apparatus, to a certain decrease in the amount of solid phase deposited on the heating surfaces. This is apparently, as already indicated, the result of the "elimination of the supersaturation" at the instant of passage of the unstable solution (water) through the magnetic field, accompanied by a release of some amount of minute crystals within the volume, which assume the role of "priming" crystals in the subsequent evaporation of the water and contribute to the crystallization. The process of evaporation of water is accompanied by a continuous removal of the carbon dioxide together with the vapor, thus ensuring continuous satisfaction of the condition of instability of the water, i.e.,  $C_{\text{CO}_2}^{\text{sol}} < C_{\text{CO}_2}^{\text{eq}}$ .

On the other hand, when working with non-supersaturated solutions, no influence of the magnetic field was observed at all.

At the present we can only formulate the aforementioned very basic conditions connected with the composition of the water treated in the magnetic field and determining the feasibility or impossibility, in principle, of any effect. Of course, there are still many unclear questions concerning the processes in question. These include, primarily, the mechanism whereby the iron oxides act on the removal of the supersaturation—whether the displacements of the ferromagnetic par-

ticles in the magnetic field are a factor that accelerates the removal of the supersaturation (in analogy with intense stirring), or whether there is some other mechanism; whether the colloidal particles of the iron oxides are themselves crystallization centers, etc.

The answer to these questions calls for further specially organized experiments.

Translated by J. G. Adashko