

## APPLICATION OF THE SOL – GEL METHOD FOR THE PREPARATION OF SOME INORGANIC ION-EXCHANGERS IN SPHERICAL FORM

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Starting from the principles of sol-gel method, developed originally for the preparation of nuclear fuels in spherical form, their application to the preparation of microspheres of various non-nuclear elements is presented. In addition to the preparative conditions of the primarily hydroxidic spheres, their conversion into other insoluble compounds such as phosphates, ferrocyanides, sulphides, etc. is described. These sol - gel products work very well as ion-exchangers; their sorption properties are quite comparable to those of the common powder sorbents, the sphere from being their main beauty. Applicability of these sorbents as well as their limitations are also discussed.

### Introduction

Organic and inorganic ion-exchangers both have certain indisputable advantages and also drawbacks. Besides their high selectivity, together with marked thermal and radiation stabilities, inorganic ion-exchangers usually suffer from unsuitable mechanical properties which cause problems, especially if they are used under dynamic conditions. The origin and further development of inorganic ion-exchangers was closely connected with the demands of nuclear technology,<sup>1-6</sup> but a number of other scientific or industrial branches have learned to utilize their favourable sorption properties.

As regards their chemical nature, the modern inorganic ion-exchangers may be hydrated oxides, acidic salts of polyvalent elements, salts of heteropolyacids, insoluble ferrocyanides or other complex compounds, and they are prepared in the majority of cases by means of precipitation from aqueous solutions. The material obtained in this way is very often voluminous and can be washed out only with difficulty. Very fine dispersion makes peptization easier and after drying the material is not

too suitable for application in the usual sorption columns because of the considerable lowering of the flow rate. Attempts to overcome this shortcoming are numerous and are all based upon a certain dilution of the powder exchanger by means of an inert carrier, enabling the increase of the column throughput.<sup>7-21</sup> Though satisfactory results have been obtained in many cases, these procedures cannot avoid, among others, a certain dilution of the sorbing material, accompanied quite often by a partial deterioration of its sorption properties.

We have tried to solve the problem by preparation of regular spheres from the ion-exchanger material without any carrier, utilizing the knowledge gathered during the investigation of sphere-shaped nuclear fuels by means of the sol - gel method.<sup>22-25</sup> This method provides primarily a hydroxidic gel,\* which can be converted secondarily into other compounds (e.g. metals, ceramic materials, other insoluble compounds). We believe the products of the sol - gel method represent a new possibility in the field of inorganic ion-exchangers, particularly with respect to their application under dynamic conditions.

### Characterization of the sol - gel processes

In general, the sol - gel method itself belongs to applied colloid chemistry. The starting solution (originally merely a sol, now sometimes also a true solution) is transformed by suitable treatment to a hydroxidic gel. It is typical for this method, though not inevitable, that droplets of the feed solution are dispersed in an organic medium to gel, so that the product has the form of regular spheres with preadjusted dimensions in the range  $10^{-3}$  to 100  $\mu$ m and satisfactory mechanical strength. The prepared gels are as a rule on the borderline between crystalline and amorphous substances, so that they often possess large surface areas with many fine and homogeneously distributed nuclei of the solid phase.

The keystone in the sol - gel process is the gelation that may be induced in different physico-chemical ways. In the American ORNL process, gelation of the droplet of a concentrated sol is accomplished by means of its dehydration, the gel being formed as a result of the increased concentration of colloidal particles of a metal ion over the gelation threshold. Another method of inducing gelation is denitration of the sol particles by means of extraction with aliphatic amines (the Italian CNEN process), leading to their cohering to a gel as a result of removal of the stabilizing

\* Under the term "hydroxidic" we understand hydroxides with inclination to ready dehydroxylation, producing in this way oxohydroxides, or hydrated oxides, all containing various proportions of molecular water. As a result, the molar ratios of their components, OH/M, O/M and H<sub>2</sub>O/M, are very ill-defined and easily influenced.

ions from the colloidal particle surface. In both cases, the gel is formed directly from the hydroxo particles of the metallic cation; nevertheless, the gel may also be formed by means of admixture of an alien gelating substance that supports the formation of an extremely fine dispersion of hydroxidic metallic particles within the organic gel ("gel-supported precipitation"). This fundamental approach was most perfectly mastered in the Italian SNAM process, in which the foreign gelating additives are the derivatives of methylcellulose in approximately 5% amounts. In the Dutch KEMA process, rapid gelation (up to 20 seconds) is reached as a result of heating the droplet to about 90 °C, because at the elevated temperature ammonia is liberated in the bulk of its volume as a consequence of the hydrolytic decomposition of urotropin added to the feed solution together with urea, which acts in the gelation process as a moderator. Some other modifications or possibilities of the presented principles exist, but up to now they have not been applied to a larger extent.

The KEMA process represents internal gelation (gelation is accomplished as a result of chemical reactions induced by means of elevated temperature inside the sphere without mass transfer across its interference); both small and large spheres may be prepared by this route. The remaining processes discussed above belong to external gelation (the incentive to gelation comes from outside, being represented by mass transfer across the interface). In the latter case a semipermeable gel layer is formed on the sphere surface, causing osmotic pressure dangerous for the sphere stability, mainly in the subsequent drying, if complete gelation was not reached in the total volume. For this reason, longer periods (up to 2 hrs) are required in the external gelation process for larger sphere diameters.

As mentioned above, the sol - gel method was developed primarily for nuclear purposes; the non-nuclear applications do not seem to be too widespread at present. One of the promising possibilities of the non-nuclear applications is inorganic ion-exchangers. It is not known which of the above variants may be more advantageous from the viewpoint of the properties of the prepared exchangers. It may be estimated only that the selection of the concrete procedure will rather depend on the chemical properties of the gelling element or on the required dimensions of the spheres. Economic considerations may also play a certain role.

#### **Sol - gel method for preparation of inorganic ion-exchangers**

Our specimens have been prepared predominantly by means of the KEMA process, but exceptionally also by the CNEN method. Even though the chemism of the internal gelation is at present far from being thoroughly understood, this does not

prevent the practical application of this method for the preparation of hydroxidic gels, with reproducible properties for a number of elements.

The gelling abilities of a considerable number of polyvalent elements have been studied in our laboratory. There have been, for instance, hydroxidic gels of Fe, Al, Cr, Si, Ti, Zr, Ge, Sn, Nb and Ta, not to mention the gels of nuclear materials.

The proper working procedure consists in mixing the initial components, as a rule in the form of their aqueous solutions, and dispersing the feed solution into an immiscible medium (paraffin oil, silicone oil, kerosene, etc.). Larger spheres of approximately millimeter dimensions are prepared in continuous gelation columns by dripping from capillaries; spheres of extremely small sizes, e.g. tens of microns, may be prepared in a usual chemical reactor equipped with good stirring. In the first case, perfectly uniform spheres may be obtained, the dimensions of which depend on the dimensions of the capillaries used, or on the intensity of their vibration. Spheres prepared in stirred reactors do not possess such a uniform size; for a given solution this depends on the density and surface tension of both liquid phases, as well as on the intensity of stirring. Quite recently, methods have been developed<sup>26</sup> that enable the preparation of monodisperse particles (droplets) of small dimensions. In every case, experience shows that microspheres prepared in stirred reactors in a simple way more or less sufficiently meet the demands on sorbents used in small and medium-size columns.

After completion of the gelation, the prepared spheres must be separated from the liquid phase and washed with an appropriate solvent (e.g. carbon tetrachloride, trichloroethylene, acetone, alcohol). In many cases it has been found convenient to finish the hydrolysis in dilute ammonia.

With regard to inorganic ion-exchangers in particular, one fact is very important, namely that the gel spheres may be transformed using appropriate reagents to another insoluble chemical form without damaging the spherical shape or deteriorating their mechanical properties considerably. This process consists in principle in exchanging the hydroxyl groups representing one of the basic components of the gel phase for other functional groups. The conversion can be accomplished by treatment with acids or acidified salt solutions. In some cases the conversion may also be performed with a gaseous reagent, e.g. with hydrogen sulfide when preparing sulfides. The time of conversion depends on a number of parameters, but as a rule, does not exceed one hour. The stability of gel spheres against peptization in these solutions is sufficient, because the spheres are not damaged after one or several days of contact.

Attempts have been made to attain a "double conversion", when after the transformation of the hydroxidic gel to an insoluble salt of the identical cation, the original cation was in turn exchanged for another one. In this case, the solubility

product of the final compound must be lower than that of the intermediate product. Even when it was found that the double conversion could in principle be realized, the preliminary results were not sufficiently satisfactory because of the imperfect mechanical properties of the obtained product.

### Merits, prospects and limitations of the sol - gel method

To the present time, we have prepared a number of inorganic ion-exchangers, some of which at least have a good chance to become commonly used in the near future. In addition to the hydroxides of polyvalent metals, mention should be made of the acidic salts of these metals, particularly phosphates, pyrophosphates, polyphosphates, arsenates, antimonates, vanadates, molybdates and tungstates, to say nothing of silica gel, and aluminosilicates. Such substances as, for example, Prussian blue and other ferrocyanides, iron(III) sulfide and substances with electron-exchanging properties, are also worth mention. In addition, some insoluble organic compounds of polyvalent elements have been prepared, not to speak of compounds that may serve for purposes other than sorption (ferrites, solid electrolytes, etc.).

Owing to the regular shape and nearly uniform size of the spheres, favourable behaviour of the sol - gel products may be expected not only in their application in standard chromatographic columns, but also in other sorption techniques, such as thin-layer chromatography, gas chromatography, fluid bed technique, etc.

For some purposes, however, the spherical form is not inevitably needed. Of course, the hydroxidic or converted gel may be prepared, for example, after soaking the initial solution into a strip of chromatographic paper or another suitable material. Similarly, a thin layer of the gel may be deposited on a glass surface. It is necessary to keep in mind in these and similar applications that after drying the prepared gel shrinks (the linear dimensions vary indirectly with the cube root of the concentration of the metal, practically by a factor of two or three, the exact value depends upon the drying conditions as well). For this reason, any inhomogeneity in the gel spheres leads to their cracking during drying. This fact will be still more important when preparing bodies with a non-spherical shape. On the other hand, it does not imply a complete deterioration of the sphere-shape in the exchanger because, as a rule, the gels do not disintegrate to powders but to several pieces, so that for some applications they could still be employed. Other methods also exist which do not exclude the application of the moist, undried gels (gel chromatography, electrophoresis, preparation of semipermeable membranes, etc.). In these cases, there is much room for research on the effect of the chemical composition of the gels on the individual processes.

For some elements, the compounds of which possess interesting sorption properties, but whose solutions have for certain reasons defied direct gelation, so that they cannot at present be used in the form of spherical ion-exchangers, other procedures should be applied. For instance, this is the case with bivalent ions such as those of manganese, copper, nickel, cobalt and lead. Not to mention the possibility provided by double conversion, in similar cases it is possible to gel solutions or suspensions containing several components, one of which yields a gel with suitable properties. In this way, for instance, spheres of molybdophosphate in silica gel were prepared, the properties of which have been described in Ref.<sup>27</sup> Similarly, successful experiments have been performed on precipitating insoluble compounds immediately in silica gel that had been saturated with the solution of the metal salt. We must emphasize, however, that the sol - gel method cannot be expected to allow preparation of a gel from any insoluble substance.

The merits of the sol - gel method products can differ with respect to their concrete application. For nuclear fuels, for instance, it is the quality of the sol - gel material (its high reactivity at elevated temperatures, and in connection with this the high density of the final product, or the extreme homogeneity in the case of multi-component systems), together with the spherical form. For other applications, e.g. ferrites and solid electrolytes, it is only the quality, regardless of the shape. For the inorganic ion-exchangers, the main merit in our view lies in their geometrical properties, the sorption properties of the sol - gel materials being at least as good as those of the classical powder ion-exchangers of the same composition. Our opinion stems primarily from the fact that the spherical form of the inorganic ion-exchangers enables their industrial utilization.

In conclusion, we should like to state that we are quite aware that the application of the sol - gel method for the production of non-nuclear materials is at present in its early stages, so that a certain period will unavoidably be needed before a more thorough and a more deeply sophisticated view of the individual facts, possibilities, and present hopes can be formulated.

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