

NMR Studies of Cement Hydration

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I. On the Chemistry of Cement

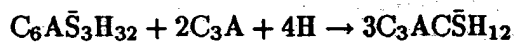
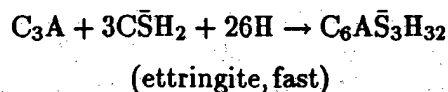
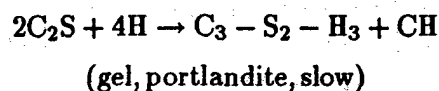
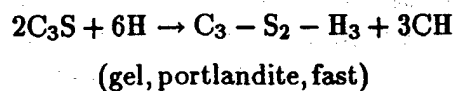
The raw materials constituting the Portland cement are mainly lime, silica, alumina and iron oxide. During the manufacturing process, a glassy quasi-crystalline clinker is formed which is ground, normally with addition of 1-3 wt% of CaSO_4 in the cement powder. This powder has four major constituents: $3 \text{CaO} \cdot \text{SiO}_2$ (in cement chemists' notation C_3S), $2 \text{CaO} \cdot \text{SiO}_2$ (C_2S), $3 \text{CaO} \cdot \text{Al}_2\text{O}_3$ (C_3A) and $4 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (C_4AF). While the proportions of these components vary, normally the cement powder consists of 60-70 wt% C, 17-25% S, 3-8% A and 0.5-6% F. Traces of MgO (0.1-4%) and alkalis (0.7-1.3), added sulphate $\text{SO}_3(\bar{\text{S}})$ and bound water (H) are also found (1).

II. On Hydration of Portland Cement

While today cement is the most widely used building material, and its first usage dates at least to the times of Roman Empire, the mechanism of its hydration is not yet that well understood. From calorimetric studies of hydrating cement, five stages could be defined (1-4). After an initial rapid hy-

dration (stage I, minutes), a dormant period is observed (stage II, several hours). Heat restarts to evolve in stage III (dozens of hours) where crystallization of CH and other crystals and formation of CSH gel takes place. Stage IV (days) is an intermediate stage where the main reaction is becoming a diffusion controlled C_3S hydration (i.e. growth of CH and CSH gel) which predominates in stage V (months, years). C_2S hydrates much slower than C_3S and in some cases reactions proceed for hundreds of years.

Chemically these reactions could be written (2) as follows:



(Ca monosulphate, slow)



(A, F)H₃

(ferrophases, fast)

These reactions, however, are only a rough approximation of the true hydration reactions of pure components. In the real system where all of the components are simultaneously present, they may take slightly different courses for this reason. The gel component (CSH) is of variable composition, which depends on local conditions. The diffraction methods yield useful information on the growth of crystalline phases (portlandite CH, ettringite, Ca monosulphate, ferro phases) but are not useful in determining the gel phase because of its amorphous structure. Understanding the structure and dynamics of CSH gel phase, however, is very important for the preparation of new types of cements with improved mechanical and resistance properties because gel constitutes the majority phase in the hardening cement paste. In this respect the understanding of the dormant period, in which on a macroscopic scale nothing changes, is essential, because there is evidence that the ultimate properties of the cement are determined in this period.

Theories of cement hydration can be divided into two groups: delayed-nucleation and protective-layer theories. The former explain the dormant period by the delayed nucleation of CH due to the retarding effect of soluble silicates (5). In order for the crystallization of CH to begin the water phase must be supersaturated with Ca²⁺. The dormant period is the time needed for the Ca²⁺ to reach the sufficient supersaturated concentration. Only when the CH crystallization begins (stage III), the calcium ions do not have to move into a solution of increasing chemical potential. This had also controlled the dissolution of C₃S before because Ca ions are removed from the solution upon crystallization. At this stage other reactions can proceed and are later on slowly dying out through Stages IV and V. In stage V, in addition to the slower reactions, predominantly C₂S hydration, and structural changes in the CSH gel, recrystallization and polymerization of silica are taking place.

As an example of the protective layer theories the osmotic model of cement hydration (6) will be described (see also Figure 1).

According to this model, cement grains, upon mixing with water, become coated with early hydration products (gel envelope). The surface of this protective cover acts as a semi-permeable membrane allowing water and smaller ions to diffuse through it, while the larger silicate anions are prevented. The water within the gel coating keeps dissolving the grain and, as a result, the concentration difference across the membrane is increasing. Consequently, the osmotic pressure builds up and it forces the water to diffuse into the gel. The end of the dormant period is characterized by the rupture of this membrane. From membrane ruptures the tubular fibrils of gel are growing. However, the water keeps on diffusing through the membrane into gel, thus dissolving the bulk grain and this supplies the material for the forming of the gel in fibrils. The fibrils from different grains eventually interlock and the hardening cement paste is beginning to develop rigidity. Simultaneously, the crystals of ettringite and portlandite are growing.

Although countless experiments were performed, it is still unclear which of the models describes better the chemical and physical processes which occur during hydration of the cement paste.

III. NMR in the Studies of Cement Hydration

Most of the NMR investigation of the setting cement pastes were ¹H studies (7). Besides protons, however, ²D, ²⁷Al, ²⁹Si, ¹⁷O, ⁵⁷Fe (Mossbauer spectroscopy) could also be used as probes in solidifying cement pastes. In recent times MAS NMR spectroscopy has also been applied (8).

Early work was on spin-spin relaxation times (T₂) of water protons by CW methods (9). Later pulsed methods were also applied (10). The proton spin-lattice relaxation times (T₁) was used to monitor the hydration of cement pastes (11). In these studies only the water, which exchanges fast between bulk water and water adsorbed on the developing cement surfaces was monitored. However, from the models we see that water protons are statically and dynamically distributed between gel components (C-S-H), crystalline products, portlandite

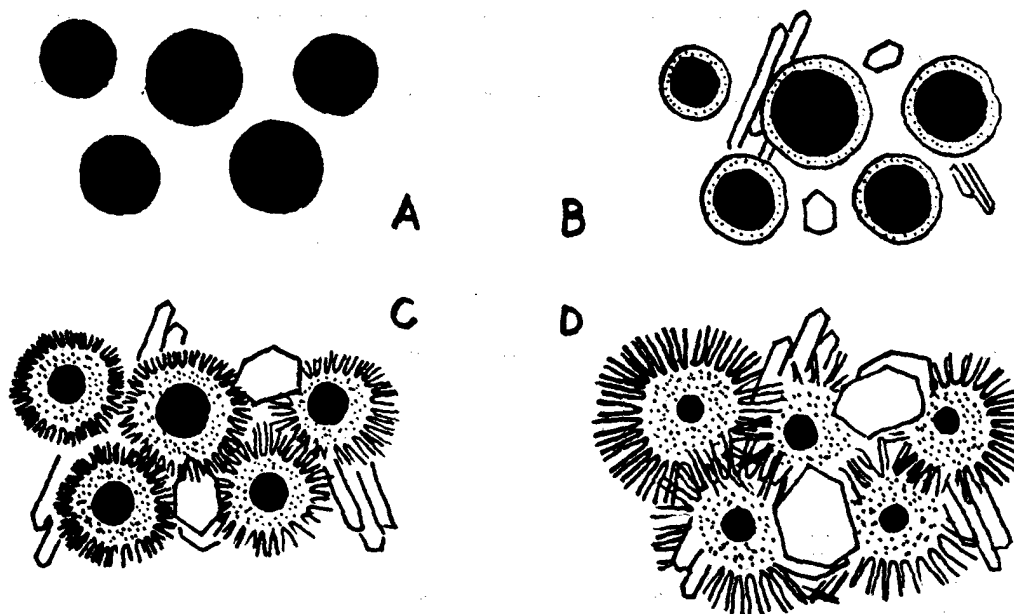


Figure 1. Two-dimensional schematic representation of the hydration of cement as proposed by the osmotic theory: a) dry cement powder b) early hydration products form gel envelope c) gel coating bursts and fibrils start to grow. Some CH (platelets) and ettringite crystals (needles) are also shown d) rigid cement networks (25,26).

(CH), calcium aluminosulphate ($C_6A\bar{S}_3H_{32}$) and others, adsorbed water molecules, and water in different pores: water in layers ($\leq 1\text{nm}$), micropores (with diameter $\sim 1\text{nm} \ll 2r < 0.1 \mu\text{m}$ due to colloidal hydrate gel porosity), water in pores ($0.1 < 2r < 1 \mu\text{m}$, pores between gel particles and other hydrates of varying morphology) and water in capillaries (i.e. interstitial holes between packed cement grains with $2r \gg \mu\text{m}$ and also large voids left by poor packing of cement grains in which water may resemble bulk water). Therefore, the NMR response from such a heterogeneous system is a complex superposition of various contributions. However, by using NMR spin grouping, the composite NMR response can be resolved in its components (12,14) which are characterized by sets of $[T_1^{(i)}$ (or $T_{1\rho}$), $T_2^{(i)}$, $M\%^{(i)}$] where $M\%$ is the equilibrium magnetization (i.e. number of protons in a particular environment) of the i -th spin group. The detailed description of this technique is in the contribution by H. Peemoeller in this issue.

IV. Results and Discussion

Normally spin grouping NMR shows two T_1 components in the early stages of hydration while at the

end of the dormant period two new components are beginning to appear (15,16). After several hours of hydration the starting two T_1 components are replaced by four T_1 components. Their values of T_1 differ more than a factor of five which makes the spin grouping analysis reproducible. In addition the $M\%$ values of each of these components are above 10% and this facilitates their determination (14-16).

A typical diagram of the time dependence of T_1 components in the solidifying cement paste is schematically shown in Figure 2. The magnetization fractions of the observed components as a function of hydration time are presented in Figure 3.

Components A, B, II, III and IV can be T_2 resolved into two components. One of them is very short with $T_2 \sim 15 \mu\text{s}$ while the second one is of the order of 1 ms (15). The value of the short one is independent on hydration time while the longer ones are fairly constant in the first ten hours and then they start to decrease and after 1 year they are between 100 and 200 μs . Their corresponding magnetization fractions can be also determined and could be found in refs. 15 and 16.

The absolute values of T_1 's and T_2 's slightly differ from sample to sample due to different content of paramagnetic ions, especially Fe^{+3} , whose concentration ranges from $\sim 2 \text{wt}\%$ in Portland cement

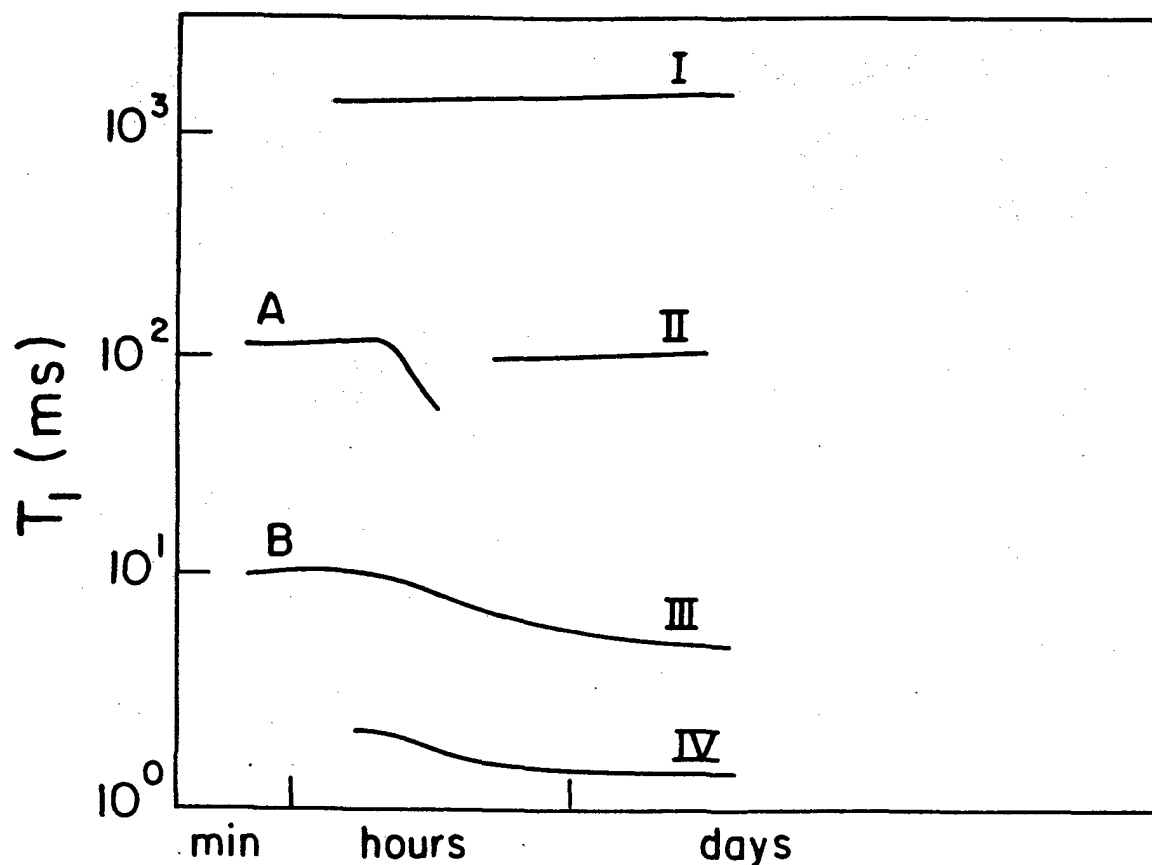


Figure 2. Evolution of T_1 components as a function of hydration time. This figure shows only the trend observed in several experiments (14,15,16,27,28). The real values of T_1 components vary as much as 50% in different experiments mainly due to the different amounts of paramagnetic impurities, predominantly iron, in the cement samples. Errors in the individual experiments are estimated to be below 5% (12,13).

to ~ 0.01 wt% of Fe in some synthetic white cements. Qualitative correlation between shortening of T_1 with increasing concentration of iron can be observed. The presence of iron (and other paramagnetic impurities) strongly influences the relaxation behavior of exchangeable water (component A, and also B, before dormant period and components II and III after). Slight differences were observed also due to different finesses of different cement, powders (i.e. specific surface area).

The proton signal of sample comes mostly from the protons of the added water. The magnitudes of the observed signals are also related to the number of protons in a particular compound and not only to the wt % of the given compound at given time of cement hydration. Therefore the proton density of the sample must be evaluated in order to understand $M\%$ ⁽ⁱ⁾ data properly.

Immediately after mixing cement powder with water, signal comes from early hydration products

and from water which is adsorbed and trapped in/on/between the gel coatings of cement grains. Water molecules, which are bonded in early gel (group B) have shorter values of T_1 as the loosely bound water molecules (group A) and which T_1 strongly decreases as hydration restarts after the dormant period. In this period several components start to grow. The easiest to determine is component I. This is portlandite (CH) which is characterized with long T_1 (~ 1 s) (and short $T_2 \sim 15 \mu$ s) due to its crystal lattice with regular structure. Its value of $M\%$ ⁽ⁱ⁾ is approaching the calculated value in the later hydration stages only slowly due to the slow reaction of the C_2S component which can last for years. At the same time the CSH gel starts to harden and according to the stoichiometry of samples and values of $[T_1; T_2; M\%]$ triplets this is component IV in Figures 1 and 2. Simultaneously crystalline products from C_3A , $CaSO_4$ and possible C_4AF are growing yielding crystals with large

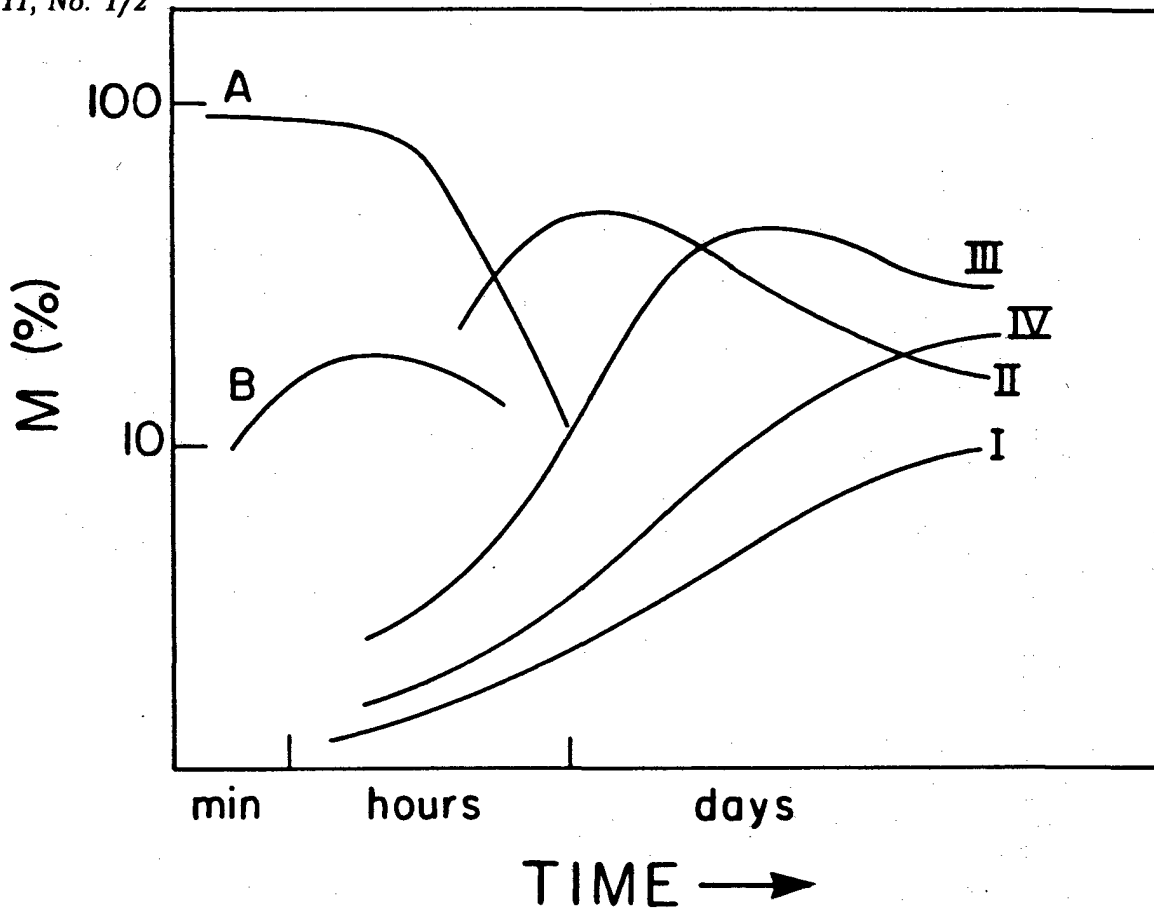


Figure 3. Time evolution of equilibration magnetizations in hydrating cement paste. Again, this is only a general picture observed in several experiments. The absolute values depend on the cement composition and w/c ratio and are published in the original publications (14,15,16). The error in each of these experiments is estimated to be below 2% (12,13).

amounts of crystalline water and therefore relative high proton fractions. This crystalline water is attributed to component II. Its decrease in later stages of hydration can be understood by the recrystallization reactions where ettringite crystals with 32 molecules of crystal water recrystallize to calcium monosulphate which has only 12 water molecules and different lattice dynamics which influences also the values of T_1 and T_2 . The remaining component III can be attributed to exchangeable (capillary) water which is adsorbed on the surface of porous cement paste, mainly on CSH gel. There are also water molecules in the micropores and gel interlayers. They are in close contact with CSH gel and crystalline products and are observed as part of components IV and II, respectively.

The extremely short relaxation time of ~ 1 ms of component IV is most likely due to a microscopic heterogeneity relaxation mechanism where water molecules are kneading through the irregular

structure of the hydrated gel where the variations in local fields are very large. Paramagnetic impurities are also believed to be adsorbed on these two-dimensional sheets (on the nm scale) of the hardened CSH gel structure. The decrease of T_1 of this component with hydration time is probably due to the hardening and growth of the gel structure which increases the local heterogeneity. The decrease in the values of T_1 of component III can be understood by the growing surface area of crystalline products. The same is true for component II (and A). The observed values of T_1 are averages of T_1 values of bound and free water $(1/T_1) = (1/T_1)_{free} \cdot f_{free} + (1/T_1)_{bound} (1-f_{free})$ where f and $(1-f)$ denote fraction of free and bound water respectively. As the specific surface area in the sample increases during the hydration so does the $(1-f_{free})$ and because $T_{1bound} < T_{1free}$ the observed T_1 decreases. This conclusion is confirmed by two T_2 values associated with each T_1 component (15). The mechanism

for this decrease in the component III is probably the exchange of magnetization between bound water and free water in its vicinity. Although cement is macroscopically very heterogeneous, microscopically these domains are well separated and there is no exchange of magnetization between different phases. The apparent increase of T_1 of component II is closely related to the drastic decrease of its M%. This means that the majority component (A) is used up in this stage and the small amount of adsorbed water ("watery gel" water, drops from 90 to 15%) still remains with the same value of T_1 .

These results show that spin grouping NMR is a usable, nondestructive method for the follow up of cement hydration. Once [T_1 , T_2 , M%] are established it can be used as a routine tool to study hydration as a function of other variables (temperature, pressure, chemical composition, additives: retarders, accelerators, superplasticizers). Such systematic studies would undoubtedly shed more light on the still poorly understood hydration process. Besides the analysis of cement hydration products these results contain also information on the kinetics of cement hardening. From the NMR data it can be shown that the osmotic model of cement setting is more likely (17).

From the above it can be concluded that the solidification of cement is a very complex process due to its heterogeneous and colloidal nature. On the other hand the recent introduction of concepts of physics of fractals into the colloid science greatly enhanced our knowledge about the aggregation behavior of these systems and it was logical to apply this new approach of describing aggregates, gel, porous material into the studies of cement hydration.

V. Cement as a Fractal System

In contrast to most of the studied objects gel and aggregates could not be satisfactorily described by the classical Euclidean geometry. The functions and curves which could describe their shape, i.e. perimeter, surface or bulkiness, are not differentiable at any point and could not be approximated satisfactorily by curves and functions from Euclidean geometry. In general they can be characterized by other parameters and the most important one is their fractal dimensionality, D , which is, roughly speaking, the measure how the fractal object is filling the space

(i.e. Euclidean dimensions $d = 1, 2, \text{ or } 3$). For instance, mass of fractal object varies with its length according to

$$m \propto l^D$$

and fractal dimension D is normally noninteger value with $0 < D < 3$ for $d = 1, 2, 3$ (18).

The concepts of irregular fractals were very useful in the understanding of gelation and structure of gels. Most of the porous objects could be, in the scale of short lengths, viewed as fractal while for larger lengths the structure becomes homogeneous due to connections between aggregates. The volume of pores of fractal structure is proportional to the number of spheres with radii R which can be packed in the voids and pores

$$V(R) \sim N_R \cdot R^3.$$

From the definition of D one gets $N_R \sim R^{-D}$ and it follows

$$V(R) \sim R^{3-D};$$

because the porosity (i.e. ruggedness) of surface is often measured by adsorption methods (variable R) one can measure surface fractals by adsorption studies since (19)

$$dV(R)/dR \sim R^{2-D}.$$

To understand the aggregation processes the experimental measurements of D (mainly by scattering, microscopic and adsorption techniques) are correlated with theoretical computer simulations. The models most used are particle-cluster and cluster-cluster aggregation. The first yields $D \sim 2.5$ while the second gives $D \sim 1.75$ for $d = 3$. These values can be, however, slightly changed by invoking reversible instead of irreversible particle/cluster-cluster sticking. By comparing theoretical and experimental values of D a fairly good knowledge about aggregation or gelation and the structure of aggregates or gels could be obtained. One of the characteristics of objects with fractal geometry is its self-similarity over many scales and the value of D can be used as a useful indicator of the complexity of autocorrelations over many scales. However, the term fractal does not imply only to spatial phenomena but also to temporal (20).

Due to its amorphous, porous, gel-like nature and similarity with porous rocks with fractal structure solidified cement was studied by neutron diffraction and it was indicated that it may be a fractal object with $D \sim 2.8$ (21,22). This result was confirmed by NMR measurements. In the NMR experiment the fractal nature could be seen by the surface induced relaxation of water molecules. In the first approximation the composite NMR response of the exchangeable water was followed. It was found that in this system the time recovery of the magnetization could be best described by the stretched exponential form (23)

$$M(t) = M_0(1 - e^{-(t/T_1)^\alpha}),$$

where the parameter α , which is between 0 and 1, determines this deviation and is related to the fractal dimensionality D

$$\alpha = D_V - D_S,$$

where D_V and D_S are the volume and surface fractal dimensions, respectively. On the other hand α can be calculated also theoretically from the percolation theory and surface to volume ratio distribution of various clusters (23). However, by spin grouping it is possible to resolve and subtract the components which are known not to be characterized by fractal geometry (CH) and to determine the fractal dimension of the remaining spin mass (24). This research is in progress.

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