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Cellular Automaton Simulations of Cement Hydration and Microstructure Development

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Abstract

Cellular automaton algorithms, which operate on a starting digital image of a water-cement suspension, are described. The algorithms simulate the microstructure development process due to hydration reactions that occur between cement and water. This paper describes the evolution of the cement model from a simple model, which treated the cement particles as single phase materials, with a greatly simplified hydration chemistry, into a model which has many more chemical species and includes numerous reactions which eventually convert the viscous water-cement suspension into a rigid porous solid.

Methods are presented for generating two and three dimensional images representing suspension initial conditions; these are derived both from micrographs of real cements and computer-based algorithms. The 2D initial images are based on the processing of backscattered electron and X-ray images of real cement suspensions. The 3D images employ either spheres to represent cement particles, or more realistic randomly shaped particles via an algorithm which smooths and thresholds a 3D lattice whose sites are initially populated with random white noise.

A convenient measure of the point at which the initial paste turns into a solid material is the percolation threshold of the solids. Consideration of these models has already led to the prediction and subsequent experimental observation of a sharply-defined onset of shear wave propagation, from ultrasonic measurements through hydrating cement slurries. The amount of hydration needed to reach the percolation threshold can be determined in the present simulations, and our results are compared with time of shear wave onset in actual cement slurries.

Variants of the basic model provide insight into both early time behaviour that is of primary interest to oil-well cementing and the later time microstructural properties that are of interest in the construction industry.

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1 Introduction

While cementitious materials are often viewed as simple "low-tech" materials, they are in fact inherently complex over many length scales. The starting material, cement powder, is obtained by grinding cement clinker. The cement clinker is manufactured by firing mixtures of limestone and clay, which contain aluminate and ferrite impurities. After extraction from the kiln, gypsum (calcium sulphate dihydrate) is added to moderate the hydration process. After grinding the clinker and gypsum, the cement powder then consists of multi-size, multi-phase, irregularly shaped particles generally ranging in size from less than $1\mu m$ to slightly more than $100\mu m$. When this starting material is mixed with water, hydration reactions occur which ultimately convert the water-cement suspension into a rigid porous material, which serves as the matrix phase for concrete, a cement paste-sand-rock composite. The nominal point of hydration at which this conversion to a solid framework occurs is called the set point.

The various chemical phases within the cement powder hydrate at different rates and interact with one another to form various reaction products. Some products deposit on the remaining cement particle surfaces (surface products) while others form as crystals in the water-filled pore space between cement particles (pore products). Moreover, some of the hydration products contain nanometer-sized pores so that the size range of interest for these materials is from nanometers to hundreds of microns, or even centimeters if one includes the aggregates (rocks) used in concrete. Due to these complexities, many unanswered questions remain in the materials science of cementitious materials. For cementitious materials, in common with most materials of industrial interest, the key relationships between processing, microstructure, and properties must be understood in order to have better control over the material in use. The approach described in this paper is aimed at elucidating these relationships.

The initial chemical composition of cement is complex as is the dynamic behaviour of the hydration process. Both aspects are not well understood at a fundamental level. A better understanding of the early age behaviour is needed in speciality applications of cements such as those arising within the oil-well industry. Cement is used to line oil wells by pumping a cement slurry between the well-bore and the steel casing inserted in the well. The cement slurry sets, forming a low permeability annulus that isolates the productive zone of the well from the rest of the formation. A slurry which either sets too quickly (while being pumped) or too slowly is a costly failure. Thus, control and prediction of the time at which the cement slurry can no longer be pumped, its *thickening time* [1], is needed. The thickening time is clearly related to the set point, as the viscosity diverges as a solid framework becomes establishes. The thickening time is controlled by an *induction period* during which very little hydration occurs. The induction period separates a short initial stage of fast but limited hydration from a somewhat slower but more complete hydration in which the cement is transformed into solid form. Additives which are known to influence the length of the induction period have been discovered empirically. For example, carbohydrates such as sugar are very effective retarders; their addition can significantly extend the thickening time, or even prevent setting completely. It is the inherent complexity of the cement hydration process that has prevented the development of a well understood theory which would allow better control of the thickening time.

Another major problem in trying to characterize the thickening time or set point in terms of microstructure is how to describe the three-dimensional microstructure of cementitious materials, since electron microscopy and similar techniques provide only two-dimensional views of the microstructure. For example, the capillary pore system (generally consisting of pores larger than about $100nm$) may appear discontinuous in a two-dimensional image while still being highly percolated in three dimensions [4]. Computer models offer a promising solution to this dilemma by allowing three-dimensional microstructures to be represented in a detailed fashion.

This paper outlines the application of a specific class of computer-based simulation models, called cellular automata, to modelling the complex process of microstructure development within hydrating cement slurries. The underlying cubic lattice for this cellular automaton (CA) is based on a two or three-dimensional digital image representing the initial conditions. The physico-chemical process of hydration is modelled by the iterative application of a series of generally probabilistic rules for updating the microstructure at any given instant of discretized time based on its current state. The underlying lattice structure of the model microstructure allows for rapid quantification of clinker phase fractions and phase connectivity [4] and the computation of physical properties such as elastic moduli and diffusivity [22, 23], which can then be compared to experimental measurements to improve the model or provide new insights into relationships between microstructure and properties. The time evolution of the model can also be monitored by quantifying the phase fractions and the chemical species at each time step in the simulation. These can be compared to measurements made by attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR). This technique can be used to conveniently monitor the evolution of the infrared spectrum of a cement sample as it hydrates [27], hence giving information on the chemical composition of the system.

A number of these issues are addressed in the present paper, which is structured as follows. Section 2 describes the CA approach to simulation, reviews the physico-chemical process of cement hydration, and shows how CA transition rules can be used to model various aspects of the process. Section 3 describes the methods we have used for creating starting images of cement slurries. Section 4 compares percolation results from our model simulations to experimental measurements on real cement slurries, and the paper concludes with a discussion in Section 5.

2 Cellular Automaton Based Cement Hydration Model

2.1 Cellular Automaton Based Simulations

A CA is a spatially and temporally discrete computer algorithm in which one or more discrete variables are associated with each site in a lattice. For our cement models, each site represents a small element (pixel) of a 2D or 3D cement microstructure. Each site in the lattice behaves as a boolean processor; the values of the variables at each lattice site - its "state" - are updated by a small set of rules which define the new state of each site based on its current state and on the current states of neighbouring sites. The rules are applied to every site in one time step and generate the new state of the system at the next step. The neighbourhood can be arbitrarily large, but it usually comprises no more than the nearest neighbours. The fact that the state variables are discrete means that the quantities they represent and derived quantities are also discrete (*e.g.* mass, momentum, velocity, etc.). In modelling systems which include moving pixels, the state identifies the type of pixel (chemical species) present at that lattice site. Only a single species occupies one lattice site at any instant of time. The movement of pixels is modelled by exchanging the state of one lattice site with a neighbour.

The approach to modelling a physical system using a CA is different from more conventional approaches. Traditionally, a model is formulated using continuum mathematics, usually in the form of a partial differential equation (PDE). Such equations are usually solved numerically, and the numerical solution involves discretization (finite difference and finite element techniques, real numbers to floating point representations, etc.). For example, in fluid mechanics, one can either work with the Navier-Stokes equations (PDEs) (continuum approximation) or molecular dynamics, in which one uses as complete a picture of the microscopic world as possible, usually Newton's equations of motion plus details of intermolecular forces. The CA approach lies between these two extremes. It is discrete in time and space (unlike PDEs before numerical solution) and it ignores the full dynamics and details of the intermolecular forces. For example, the coarse-grained macroscopically averaged behaviour of one class of CA, "lattice gases", obeys the hydrodynamical equations of motion for an incompressible Navier-Stokes fluid (at least for low Reynolds numbers) [40]. Since the Navier-Stokes equations are used to model flow in a wide range of viscous fluids with very different intermolecular forces, it is evident that much of the detailed nature of these forces is irrelevant in determining fluid flow patterns. Thus one avoids describing in complete detail all the physical and chemical processes that occur when using CA. Instead, one attempts to find the *simplest* microscopic model which shows, as far as is possible, the complete spectrum of macroscopic behaviours of the real system being modelled.

Though a "pure" CA exclusively uses rules which change the state of a site based on a boolean function of the states of its *local* neighbours, it is often useful to use less constrained rules for simulation applications. Sometimes rules are used which update many sites or make use of non-local information, for example, a global test flag or a globally computed concentration of a given species (i.e. total number of sites in a given state). Rules may include any computable function on the state as desired. The advantage of pure CA is that their architectures are inherently parallel and they therefore offer the potential of being run on parallel computers very efficiently [11, 26]. The use of rules which access non-local information can be supported by specialized machine hardware or can be replaced with rules which produce similar effects but only require local information, and thus the parallelism of the CA program can be maintained.

A well-known feature of CA computations is their ability to produce surprisingly complex behaviour from very simple rules. A CA can produce a range of periodic, chaotic and generally very complex behaviours with intricate spatial and temporal patterns [39]. Such features are attractive in modelling a system as complex as a hydrating cement slurry.

2.2 Cement Chemistry

As with the development of any cellular automaton type model, rules must be selected to govern the state transitions occurring at each lattice element (site) of the microstructure. For cement, this requires a detailed understanding of the chemical reactions occurring when cement reacts with water. Review articles describing cement chemistry are available [14, 25, 34] but, as will be outlined below, a well defined quantitative account is still lacking. This section provides a generally plausible outline of cement hydration, which should be viewed as a simplification of the more detailed and poorly understood processes taking place in real cement. For example, the composition of the cement particles is conventionally broken down into several pure phases, but this is an idealization. Real particles may have regions which are not pure, but are hybrids of different proportions of silicate, ferrite and aluminate; in oilwell cements the situation is particularly complicated [9]. The "true" chemical composition of the cement phases remains an open question. Attempts have been made since the time of Bogue [12] to predict such phase compositions starting from oxide analyses of the original clinker but, although these predictions are still widely used, *e.g.* for furnishing American Petroleum Institute (API) specifications of oil well cements, they can only be regarded as approximations. The amorphous gels and crystalline products produced during hydration may also have a variety of chemical forms [38].

The most widely used cement is portland cement. The four major Bogue clinker phases present in portland cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF); the clinker is ground with gypsum ($C\bar{S}H_2$), where the following conventional cement chemistry notation is used: $C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, \bar{S} = SO_3$, and $H = H_2O$. Densities and molar volumes for all phases relevant to our models, taken from the cement literature [30, 31, 41], are given in Figure 1.

The reactions used in our cement microstructure models are summarized in Figure 2. The numbers below each reaction equation indicate the volume units of each phase required to balance that particular chemical reaction. Knowing the molar volumes and the reaction stoichiometries, these volume stoichiometries can be easily calculated for each reaction. Since Bogue phases are only approximations, so too are these idealized cement hydration reactions. Indeed, there is considerable controversy in the cement chemistry literature concerning what reactions are actually occurring, which are slow or fast, what are the mechanistic details, and even the exact chemical composition of the species that may exist during hydration. It is a virtue of the CA approach that we can deliberately avoid pursuing an overdetailed chemical description, and still obtain realistic physical properties of the evolving dynamical system.

As seen in Figure 2, the silicate reactions are simpler than those for the aluminate and ferrite phases of portland cement. Tricalcium silicate is the major component of portland cement; it is generally present in a mass fraction of 50-70%, and is considered to be responsible for controlling many of the ultimate properties of cement-based materials including transport and strength properties. When C_3S reacts with water, a nanoporous, amorphous calcium silicate hydrate ($C{-}S{-}H$) gel is redeposited on the surfaces of the original C_3S and and on previously deposited $C{-}S{-}H$, while calcium hydroxide (CH) crystals nucleate and grow in the available capillary pore space. As time proceeds, the $C{-}S{-}H$ gel polymerizes, but we do not include this process in our list of reactions. The reactions for C_2S are similar, but less CH is formed due to the lower Ca/Si molar ratio of the initial C_2S. Additionally, in portland cement, the C_2S typically reacts at a much slower rate than the C_3S. Due to the extensize use of pozzolanic materials such as silica fume and fly ash in concrete, the pozzolanic reaction between calcium hydroxide and reactive silica has been included in the list of reactions. The stoichiometry for this reaction is based on recently published data [30] and is an approximation as it is likely to vary with water-to-cement (w/c) ratio and silica fume content.

Tricalcium aluminate, C_3A, is generally the fastest reacting phase in portland cement. In fact, gypsum is specifically added to portland cement to slow down this reaction, thus avoiding "flash set" of the material. When gypsum is not present in the system, C_3A reacts with water to form a variety of crystalline hydration products, with hydrogarnet, C_3AH_6, being the ultimately stable hydration product. Because the aluminate phase is critical to early hydration

Compound Name	Compound Formula	Density (g/cm^3)	Molar Volume $(cm^3/mole)$
Tricalcium silicate	C_3S	3.21	71
Dicalcium silicate	C_2S	3.28	52.4
Tricalcium aluminate	C_3A	3.03	89.1
Tetracalcium aluminoferrite	C_4AF	3.73	128
Gypsum	$C\bar{S}H_2$	2.32	74.2
Calcium silicate hydrate	$C_{1.7}SH_4$	1.85	124
Pozzolanic $C-S-H$	$C_{1.1}SH_{2.1}$	1.97	81
Calcium hydroxide	CH	2.24	33.1
Ettringite	$C_6A\bar{S}_3H_{32}$	1.75	715
Monosulphate	$C_4A\bar{S}H_{12}$	1.99	313
Hydrogarnet	C_3AH_6	2.52	150
Iron hydroxide	FH_3	2.2	95.2

Figure 1: *Densities and molar volumes of cementitious materials*

Silicate Reactions

$$\begin{array}{ccccccc} C_3S & + & 5.3H & \rightarrow & C_{1.7}SH_4 & + & 1.3CH \\ 1 & & 1.34 & & 1.75 & & 0.61 \end{array}$$

$$\begin{array}{ccccccc} C_2S & + & 4.3H & \rightarrow & C_{1.7}SH_4 & + & 0.3CH \\ 1 & & 1.49 & & 2.39 & & 0.191 \end{array}$$

$$\begin{array}{ccccccc} 1.1CH & + & S & + & H & \rightarrow & C_{1.1}SH_{2.1} \\ 1.34 & & 1 & & 0.67 & & 3.0 \end{array}$$

Aluminate and Ferrite Reactions

$$\begin{array}{ccccc} C_3A & + & 6H & \rightarrow & C_3AH_6 \\ 1 & & 1.21 & & 1.69 \end{array}$$

$$\begin{array}{ccccccc} C_3A & + & 3C\bar{S}H_2 & + & 26H & \rightarrow & C_6A\bar{S}_3H_{32} \\ 0.4 & & 1 & & 2.1 & & 3.21 \end{array}$$

$$\begin{array}{ccccccc} 2C_3A & + & C_6A\bar{S}_3H_{32} & + & 4H & \rightarrow & 3C_4A\bar{S}H_{12} \\ 0.249 & & 1 & & 0.1 & & 1.31 \end{array}$$

$$\begin{array}{ccccccccccc} C_4AF & + & 3C\bar{S}H_2 & + & 30H & \rightarrow & C_6A\bar{S}_3H_{32} & + & CH & + & FH_3 \\ 0.575 & & 1 & & 2.426 & & 3.21 & & 0.15 & & 0.43 \end{array}$$

$$\begin{array}{ccccccccccc} 2C_4AF & + & C_6\bar{S}_3H_{32} & + & 12H & \rightarrow & 3C_4A\bar{S}H_{12} & + & 2CH & + & 2FH_3 \\ 0.358 & & 1 & & 0.302 & & 1.313 & & 0.093 & & 0.266 \end{array}$$

$$\begin{array}{ccccccccc} C_4AF & + & 10H & \rightarrow & C_3AH_6 & + & CH & + & FH_3 \\ 1 & & 1.41 & & 1.17 & & 0.26 & & 0.74 \end{array}$$

Figure 2: *Cement model reactions - numbers indicate volume stoichiometries*

properties, it is of great interest in oil-well cementing. Reactions are much more complex in the presence of gypsum. In this case, the C_3A will react with the gypsum to form ettringite, $C_6A_3\overline{S}H_{32}$, whose crystals are often observed to grow as needles within the cement paste. Microscopic analysis has shown the wide range of morphologies of growing ettringite crystals and their sensitivity to clinker phase proportions and ambient conditions [28]. When all of the gypsum is consumed, the ettringite may decompose, reacting with more of the C_3A to form the monosulphate phase, $C_4A\overline{S}H_{12}$. Additionally, ettringite is unstable above 60^oC, exemplifying that cement reactions are a function of temperature as well as solution concentrations. Ambient conditions are assumed in this paper. The sulfate ions are generally more mobile than the aluminate ions so that ettringite forms either in solution or at the surfaces of the aluminate phases in cement paste. There is also evidence that the ettringite changes from a gel to a crystalline form during cement hydration: application of ATR/FTIR techniques to measure changes in chemical composition during hydration does not indicate any $C-S-H$ formation at early time, but the attainment of a steady level of ettringite (though this does not preclude a phase change of ettringite, such as from gel to crystalline form) [27].

The reactions of the ferrite phase, C_4AF, are the least well understood of those occurring during portland cement hydration. The ferrite phase generally reacts slowly (in comparison to the other phases) and only contributes to long-term properties of cements (although exceptions to this have been noted in the presence of special additives [18], and the aluminate/ferrite ratio does have a strong effect on thickening time in oilwell cements). In the present work, we have assumed that the reactions of the ferrite phase are similar to those of tricalcium aluminate, with the production of extra calcium hydroxide and iron (III) hydroxide FH_3 to account for the extra calcium and iron present in the C_4AF phase, based on experimental evidence given by Brown [13]. No density information was available in the literature for the iron hydroxide gel forming in cement paste, so the value of $2.2g/cm^3$ given in Figure 1 was assumed.

Cement hydration does not proceed at a fixed rate. The evolution of hydrating cement can be qualitatively characterized by the heat evolution curve sketched in Figure 3 [32]. The process can be broken down into five stages: (1) preinduction, (2) induction, (3) acceleration, (4) deceleration and (5) diffusion limited.

Figure 3: *Hydration Stages*

The major activity during each stage is described qualitatively as follows:

1. Preinduction - This is the initial rapid hydration that occurs when the particles of cement are exposed to water, releasing a large amount of heat. Duration: On the order of minutes.

2. Induction - A period of reduced hydration activity. The reason why the hydration is inhibited during this time period is not clear, although many theories have been proposed. Duration: On the order of one to two hours.

3. Acceleration - The rate of hydration increases. This is the beginning of the period during which the cement paste will achieve set. The major portion of the silicates hydrates and the cement solidifies. Duration: On the order of hours.

4. Deceleration - The hydration rate decreases as the hydrated material covers the particles. Duration: On the order of hours to days.

5. Diffusion Limited - Hydration and aggregation occur at a very low rate. Reactions are limited by the rate of diffusion of species through the dense pore network. Duration: On the order of days to years.

The *set point* of a cement slurry can be defined operationally as the condition when the hydrating cement system provides a measurable resistance to penetration; a standard test for set time of hydraulic cement is given in ASTM C191 [2]. In oil-well cementing the analogous measure used is the thickening time. It is defined as the time taken to reach a certain torque when stirring a cement (in a "consistometer"). The measurement determines how long a cement slurry can be pumped; details of the standard test are given in the API standard *API Spec 10* [1]. Both measurements are designed to meet engineering needs, but relating results to simple underlying physical transformations that occur during hydration is difficult; a recent study by Chen and Odler provides a valuable discussion of this subject [17]. Our model, however, suggests a new measurement can be directly related to percolation: as the particles of cement become covered in $C-S-H$, a point in time is reached at which a continuous solid structure has percolated throughout the cement paste [4]. The model provided the insight that the percolation transition might be quite sharp, and that beyond this point the cement slurry should be able to support shear stresses, and thus permit shear wave propagation. The CA-based model suggested an ultrasonic shear wave experiment, which has subsequently been performed, confirming these conjectures [19]. The similarity between the onset of percolation in the CA model and the onset of shear wave propagation in ultrasonic experiments is discussed further in Section 4.

2.3 Transition Rules for Simulating Chemical Reactions

Cement hydration is modelled as a three part process: 1) material dissolves from the original cement particle surfaces, 2) diffuses within the available pore space, and 3) ultimately reacts with water and other dissolved or solid species to form hydration products through aggregation. Therefore, in order to simulate the microstructure development of hydrating cement, the physical processes of dissolution, diffusion, and reaction must be simulated. Each of these processes may be conveniently simulated using cellular automaton-type rules as outlined in a general way below.

Dissolution - A pixel belonging to a soluble phase may dissolve by attempting a one-step random walk to a neighbouring pixel. If the neighbouring pixel is empty (i.e. representing pore space), the dissolution is allowed and an appropriate diffusing species is created. Otherwise, the pixel remains in its current solid state. This simple rule has the desired effect surfaces with high curvature will dissolve at a faster rate than low curvature surfaces, and thus smaller particles will dissolve faster than larger ones. To control relative dissolution rates, each soluble phase can also be assigned a dissolution probability between 0 and 1. Comparing these dissolution probabilities to randomly-generated uniform deviates will allow phases with a higher dissolution probability to dissolve at a faster rate. Thus, these probabilities represent relative mass transfer rates at the particle surfaces. In this manner , the hydration can be tuned such that C_3A reacts faster than C_3S, which reacts faster than C_2S and C_4AF, in agreement with experimental observations.

Dissolution can be globally prohibited via the assignment of a dissolution flag for each phase. Only those phases with a dissolution flag value of 1 are soluble in any given time step (update or execution) of the cellular automaton. For example, ettringite's dissolution flag might be originally assigned a value of 0 but updated to a value of 1 when the majority of the gypsum (say 90%) has been consumed by hydration reactions. Alternatively, dissolution may be locally inhibited by checking for the presence of a particle of some type in the local vicinity (such as a $5 \times 5 \times 5$ cubic neighbourhood) of the pixel undergoing dissolution.

Since the hydration products generally occupy a larger volume than the solid reactants, a volume correction step is often necessary to maintain the appropriate reaction stoichiometry. For example, when a pixel of C_3S dissolves, 1.7 diffusing $C-S-H$ species and 0.61 diffusing CH species should be created according to the reaction given in Figure 2. This volume correction can be performed by adding in extra diffusing species using a random probability based on the required volume stoichiometry. The extra diffusing species may be added near the dissolution site to simulate a low species mobility or may be randomly scattered throughout the solution volume to represent an effectively infinite species mobility. Specifically, in this work extra $C-S-H$ diffusing species are added in the local vicinity of the dissolution site due to low mobility of the silicate species while extra diffusing CH species are added at random pore locations to simulate the higher mobility of the calcium and hydroxide ions.

Diffusion - Possible diffusing species created by a dissolution process include diffusing CH, diffusing $C-S-H$, diffusing C_3A, diffusing gypsum, and diffusing FH_3. To implement diffusion, each diffusing species present in the microstructure is allowed to execute a one-step random walk to a neighbouring pixel. If the neighbouring pixel is pore space, the diffusing species is transferred to this new location; otherwise, it remains at its original location. The relative rate of diffusion of a particular species can be enhanced by increasing the number of spacings in the lattice to which it may move in one time step or decreased by decreasing the probability that the species is allowed to move at all in a given time step. The diffusing species continue to undergo this random Brownian motion until reaction occurs according to the rules outlined below.

Reactions - To model cement hydration, several types of reactions must be considered. Several of the hydration products (CH, FH_3, and C_3AH_6) form by nucleation and growth processes. To simulate the nucleation processes, a diffusing species is assigned a certain probability of changing to its solid form without the presence of a surface onto which to aggregate. This probability (p) is made to be exponentially dependent on the number of diffusing species in solution (c):

$$p = p_o(1 - e^{-c/c_m})$$

where p_o and c_m are constants. This functional form gives a nucleation probability that will decay rapidly as c becomes much less than c_m so that few new crystals will form late in the hydration. The nucleation rate of one diffusing species could even be made dependent on the concentration of an entirely different diffusing species to maintain the correct solution thermodynamics (involving solubility products, etc.). Although we do not consider the possibility in the current model, nucleation can also be spatially inhibited;

for instance, CH nucleation could be inhibited in the vicinity of solid $C-S-H$ to force the CH to form "away from" the $C-S-H$ material.

Other reactions require a collision of two species in order for a reaction to occur. Examples are the deposition of $C-S-H$ on silicate surfaces and the reaction of diffusing gypsum and aluminate species to form ettringite. Here again, when a collision does occur, a probability can be specified as to whether a chemical reaction also takes place so that "bimolecular" reaction rates can themselves be adjusted within the model. Depending on the precise reaction, volume correction may not be possible during dissolution and may have to be executed when the reaction occurs. To do this, neighbouring pore pixels are converted into the appropriate solid hydration product to satisfy the needed reaction volume stoichiometry. For example, when diffusing gypsum reacts at an aluminate surface, on average, 3.21 pixels of ettringite must be created. The fractional portion (0.21) extra pixels of ettringite can be realised by using the appropriate probability to form 3 units of solid ettringite 79ettringite 21cannot be handled *a priori* during dissolution since several subsequent reactions are possible for diffusing C_3A species.

Figure 4: *Diagram of transitions between species*

The processes included in the microstructure development model can be conveniently summarized in a state transition diagram such as the one shown in Figure 4. Here, arrows indicate a change of state with dissolution, nucleation, and collision (leading to bimolecular chemical reaction) being the possible transition processes. Diffusing species are indicated with an asterisk and the dependence of a process on a variable is indicated by function notation. For example $f([CH*])$ indicates that a process depends on the diffusing CH species concentration. Periodic boundary conditions were used in all our models – no special conditions were needed in our CA rules to deal with edge effects.

The computer generated microstructure that develops when the model is executed to various degrees of hydration can subsequently be used to compute physical parameters such as the diffusion rates of ions through the pore structure, thereby providing insights into the long term behaviour of concrete [3, 23]. It should be noted that CA-type rules can just as easily be developed to model the later degradation of cement paste microstructure [5] as they can be used to model its original formation during hydration, which is the primary focus of the present paper.

2.4 Transition Rules for Early-Time Behaviour and Simulating Induction

The original program described above is somewhat unphysical in that there is an outer execution loop in which pixels on the surface of a cement grain are dissolved into solution and an inner execution loop in which the dissolved species diffuse by random walk statistics until they have all reacted. The outer loop repeats until no more surfaces of C_3S are exposed to pore space and no more dissolution can take place. The nesting of the diffusion-aggregation loop within the dissolution loop makes the program computationally simple and efficient and is an effective way of reaching the final microstructural state of the system. From the point of view of modelling the temporal evolution of cement hydration, however, the nested loops make the problem of relating model time to real time more difficult. Thus, the program was modified to contain only a single loop so that pixels dissolve, diffuse and aggregate simultaneously in every step. The relative rate of dissolution *vs.* diffusion was controlled by assigning appropriate relative probabilities of dissolution and diffusion to different species.

This program was applied to simulating the induction period found in setting cements by adding a pair of rules, one to create a species which had the effect of blocking the aggregation of diffusing $C-S-H$ onto the cement particles and another to transform the blocking species into a non-blocking one. The rule for C–S–H was also modified to test for the presence of such a blocking species in its neighbourhood; if it is present the diffusing C–S–H does not aggregate. The rate of transformation to the non-blocking form was a sigmoidal function, dependent upon the amounts of other reacting species in solution. This has the effect that as the concentration of the blocking species suddenly decreases, the aggregation restarts quickly; the new rate is faster because of the higher concentration of diffusing $C-S-H$ present in the pore space and the greater surface area of aggregation sites in the form of partially dissolved particles. Though the exact mechanism which slows hydration and precipitation of C–S–H is not known we included these rules to produce the desired overall effect. A candidate for this blocking species is the initial amorphous gel form of ettringite and its subsequent transformation into a crystalline form. Evidence for this mechanism, which comes from ATR/FTIR spectroscopy, is discussed in [10]. The state transition diagram for these rules is given in Figure 5: diffusing gypsum ($GYP*$) reacts with diffusing aluminate (C_3A*) forming ettringite ($ETR*$) which aggregates ($ETR(gel)$), and then transforms into crystals ($ETR(crystalline)$). $ETR(gel)$ is the species providing the blocking mechanism. While controversy still surrounds the mechanisms responsible for the induction period, this simple example illustrates how such behaviour can be easily realised in a CA model.

Figure 5: *Diagram of additional transitions for induction*

A complementary approach to modelling the induction period that has recently been investigated is a "chemical clock" model based on an inhibited auto-catalytic nucleation mechanism [10]. This work draws on a small set of physicochemical transformations involving the conversion of gelatinous ettringite into the crystalline form. Rate equations are developed which describe the kinetics of these processes. One step within the scheme, in particular, involves autocatalysis: conversion of the gel to the crystalline form is accelerated by the presence of crystals of ettringite. Analysis of the corresponding non-linear differential equations shows that an appropriate selection of rate constants for the reactions can produce non-linear growth in species concentrations, of the kind observed with the induction period in cement hydration. The CA approach is inherently semi-empirical in that the transition rules and probabilities are chosen in order to create the observed behaviour, while in the chemical clock approach certain aspects of the system can be derived from well established *a priori* laws of chemical kinetics. However, the simple clock model [10] has the disadvantage of requiring the assumption of spatial homogeneity, while the CA incorporates the inhomogenous nature of the evolving microstructure.

2.5 Transition Rules for Controlling Ettringite Product Morphology

As was mentioned earlier, there is evidence that the initial precipitation of ettringite is a gel which transforms into needle shaped crystals due to the nucleation process modelled in [10]. Since random aggregation generally forms isotropic structures, we have developed special rules to ensure that ettringite grows as needles [28]. Two approaches have been applied to date.

One approach is to label the head of a growing ettringite "crystal" as a special state and only allow diffusing ettringite species to aggregate onto the head of the crystal, or to make the probability of aggregating on the head higher than on other sites. Thus, three states are used to represent ettringite: diffusing, solid, and solid at the head of a crystal. When further aggregation occurs at the head of the crystal, the new solid ettringite pixel is labelled as the head of the ettringite crystal and the former head is simply labelled as solid ettringite. Figure 11 shows a 3D visualization of the single pixel thickness needles that can be generated.

A second approach is to utilize a surface curvature measurement algorithm originally developed for simulating the sintering of ceramic powders [7, 33]. By counting the number of pore space pixel neighbours, a measure of local curvature can be obtained [7]. By evaluating the local curvature at prospective ettringite growth sites, ettringite crystal growth can be biased towards pixels with a high local curvature, causing needle-like structures to form. The amount of bias can be used to control the variability allowed in the morphology of the ettringite crystals, with no bias corresponding to the totally random growth used for other "crystalline" hydration products such as CH and FH_3. Planar ettringite crystals could be produced in a similar fashion by specifying an orientation and appropriately biasing the aggregation process.

3 Generation of Initial Digital Images of Cement Microstructure

One of the inherent advantages of a CA for modelling cement microstructure development based on digital images is its capability of handling complex particle shapes and chemical phase distributions. These features are much more difficult to capture in continuum-type models where particles generally must be described as simple geometric objects such as spheres or ellipsoids, as used in [37]. For digital image-based models, however, the complexity of the cement particles is limited only by the resolution of the underlying lattice. For the simulations described in this paper, the scale of the models is such that each site is about $1\mu m$ on a side. While creating particles of essentially arbitrary complexity is relatively straightforward, generating particles which accurately represent an actual cement is a more formidable task. This section describes three methods we have used to create starting images.

3.1 Initial 2D Images Derived from Cement Micrographs

Recently, techniques have been developed to accurately capture the detailed features of multiphase cement particles [8], in two dimensions. To obtain an image of an actual cement, the cement to be characterized is dispersed in a low viscosity epoxy which is subsequently cured. The sample is polished and a $100nm$ thick coating of carbon is evaporated onto the polished surface to eliminate specimen charging in the scanning electron microscope (SEM). In the backscattered electron (BE) image, an example of which is shown in Figure 14, brightness is proportional to the average atomic number (Z) of a phase.

In the BE image, the ferrite phase appears brightest followed by the tricalcium silicate phase. Unfortunately, tricalcium aluminate, dicalcium silicate, and gypsum all exhibit similar brightnesses and thus cannot be identified on the basis of the BE image alone. To alleviate this problem, X-ray images are collected from the same area being viewed by the BE detector. Separate X-ray images are collected and thresholded for sulphur, calcium, iron, and aluminum as shown in Figure 15. By combining these four X-ray images with the original BE image, each of the four major (Bogue) phases of a portland cement powder along with gypsum may be distinguished. For instance, the presence of iron in the X-ray image indicates the ferrite phase while the presence of aluminum but not iron indicates the tricalcium aluminate phase. Similarly, the presence of sulphur indicates gypsum. Tricalcium silicate and dicalcium silicate are distinguished on the basis of brightness of the BE and calcium X-ray images. In cases where this separation is still difficult, a silicon X-ray image can be obtained and also used in the segmentation process. Finally, the segmented image is filtered using a median filter to sharpen the phase distinction in the final image and overcome some of the noise present in the BE and X-ray images. In the median filter, each pixel in the image is reassigned to be the phase occupied by the majority of its neighbours, excluding porosity, if this majority value exceeds a preset limit.

After combining the five images shown in Figs. 14 and 15 and applying the median-type filter, the final image of the cement particles (segmented into four clinker phases plus gypsum) shown in Figure 16 is obtained. This image can be used as input for a two-dimensional CA model. Accurately capturing the complexity of the starting cement material in this fashion greatly enhances the realism of the hydration model and allows it to be applied to complex real world problems requiring knowledge of the distribution of each phase in a specific cement. Examples include the study of sulphate attack, where sulphate ions infiltrate a cement-based material and undergo expansive reactions with only the aluminate and CH phases of the hydrated cement, and the diffusion and binding of chloride ions in a cement paste [6].

3.2 Synthetic 3D Initial Images Based on Spheres

While two-dimensional microstructure models are adequate for demonstrating hydration and examining microstructural features such as interfacial zones [24], three-dimensional microstructures are needed to accurately examine properties such as phase percolation and transport coefficients. Generating realistic starting microstructures (images) in three dimensions is a non-trivial task. One approach is to simplify the problem by considering the cement to be a single pure phase, similar to C_3S, the major component of portland cement, and generating digitized spheres of a specific size distribution to represent the starting cement powder in water. This simplified approach has been shown to produce realistic microstructures and has provided new insights into percolation and diffusivity properties of cementitious materials [4, 23]. More realistic chemical phase information must be built in to accurately simulate early-time hydration (before the set-point) in high aluminate cements, which is controlled by the aluminate phases [14, 17, 34]. A fast and simple way of making the spheres multiphase is by simply converting all solid pixels which are in each nth plane to C_3A, where $1/n$ is the desired proportion of aluminate.

3.3 Synthetic 3D Initial Images Based on Filtered White Noise

We have also developed a more sophisticated means of creating 3D images which produces more realistic initial particle shapes. The algorithm is derived from previous work concerned with the development of synthetic 3D models of porous carbonate rocks in which both the solid matrix and pore space are percolating over a wide range of porosities [21]. It was found that a 3D image of striking visual resemblance and similar statistical properties to real carbonate rocks could be generated by thresholding suitable Gaussian convolutions of 3D random white noise images. By raising the threshold level, we can generate non-percolated data sets of irregularly shaped particles. In order to obtain the desired water-cement ratio, the algorithm is repeatedly invoked to generate new particles which are accumulated into one 3D image if they do not intersect any existing particles. The algorithm used is sketched in Figure 6. The output of this algorithm is shown in the 3D visualization of Figure 12. A partially hydrated data set with irregular particles composed of two phases, C_3S and C_3A, using the simple method of marking the nth plane is shown in Figure 13. In both figures, the visual appearance of these grains is quite like that of real cement particles. Intuitively, this is not an unreasonable result, since cement grains are produced by the essentially random process of smashing large lumps of clinker after they emerge from the kiln. It would be perfectly possible to perform a statistical analysis of the particle size distribution and attempt to adjust the parameters within the algorithm to ensure close agreement with corresponding experimental data; we have not, however, done this in the present work. This flexible algorithm for generating random particle shapes and size distributions may be of potentially wider significance in computational materials science than solely for describing cement grains.

Figure 6: *Algorithm for creating randomly shaped initial particles*

To obtain more realistic multi-phase particles, such as those in the real 2D images, the process of accumulating particles can be modified so that when intersecting particles are detected, the overlap could be assigned to one of the other phases. This would produce irregularly shaped particles composed of irregularly shaped phases. 2D sections of 3D images produced in this way could then be cross-checked with the 2D images obtained from the BE/X-ray method described earlier. Such comparison would be necessary to determine the combination of convolution/thresholding needed to produce multi-phase particles with the correct morphological features.

4 Results

This section presents results of simulations made on the CA model and compares them to experimental measurements obtained on real cements. The simulations were performed on a variety of lattices sizes, varying from $64 \times 64 \times 64$ for fast experimentation to $200 \times 200 \times 200$

for the largest runs. A $128 \times 128 \times 128$ system typically took 3-4 hours for complete hydration on a Sun Sparc 2 workstation [2].

4.1 Microstructure *vs.* Time.

Figures 17 and 18 show the results of applying the CA hydration algorithm to the original microstructure of Figure 16 (w/c=0.672) to achieve degrees of hydration of 30% and 76%. From these figures, the capability of the CA code to generate complex microstructures based on the iterative application of relatively simple rules should be manifest.

In these figures, a yellow layer of $C-S-H$ gel can be seen forming around each of the cement particles (particularly the silicate regions of these particles). We believe that it is the formation and interlinking of these growing layers which leads to the setting of the cement pastes; this is supported by recently published experimental evidence [17] as well as our ongoing work using ATR/FTIR spectroscopy. The randomly-formed pore products would require a much larger volume of product to percolate as they do not attach specifically to the existing framework of cement particles. Thus, their contribution to the onset of solids percolation should only be significant in cements containing large quantities (more than 20 percent) of tricalcium aluminate which hydrates rapidly. For most conventional cements, then, set will ultimately be controlled by the production of the $C-S-H$ gel.

4.2 Determination of the Percolation Transition

To assess the set point, which we define rigorously as the point where percolation of solids occurs, we use a three-dimensional model based on monophase C_3S particles, thus avoiding the problem of starting with realistic 3D cement phase distributions. This simplification is justified by our assumption that the $C-S-H$ surface product causes set and by the fact that this simple model generates almost the same quantity of surface products as those produced in real cements [4].

In the model, to assess percolation, a "burning algorithm" [36] is utilized. This algorithm searches for a path across the 3D microstructure composed exclusively of the unreacted cement and $C-S-H$ phases, proceeding iteratively from each such pixel to its nearest neighbours. We uniquely label each cement particle and allow the "burning" to spread within any given cement particle and from any cement particle to $C-S-H$, and *vice versa.* Since the burning does not proceed directly across unreacted cement grains, this computational algorithm eliminates the problem of initial particle-to-particle contacts in a digital-image-based model which would result in very low w/c ratio pastes being "set" before any hydration occurs since the particles themselves will form a connected backbone. The burning starts at the top of the microstructure and continues until no more "fuel" remains, at which point we check to see if the bottom has been reached and if so, how many pixels are in the connected cluster (i.e. the fraction of solids connected). A plot of the fraction of solids connected *vs.* degree of hydration is shown in

[2] Certain commercial equipment is identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipement is necessarily the best available for the purpose.

Figure 7 for a w/c ratio of 0.35 and a particle size distribution measured on a real cement [20]. As expected, the fraction connected begins at 0 and approaches a value of 1 as the hydration progresses.

Figure 7: *Percolation of $C_3S + C-S-H$ vs. Hydration*

The amount of hydration needed to achieve set would be expected to vary with w/c, as there are different initial solids fractions. Results for various values of w/c are presented in Figure 8 which shows the amount of $C_3S + C-S-H$ present at set *vs.* w/c ratio. Higher w/c ratio values require more hydration to achieve set since the cement particles are initially spaced farther apart in the 3D microstructure. The results shown are in quantitative agreement with the recent experimental results of Chen and Odler who measured the porosity of cements pastes of various w/c ratios [17] at the beginning and end of set [2]. The actual solids percolation point probably occurs before the beginning of set as defined in the ASTM standard [2]. The results shown in Figure 8 are for several particle size distributions ranging from monosize cement particles to the particle size distribution corresponding to that of a real cement [20].

Figure 8: *Set Point vs. W/C Ratio*

Drawing upon our viewpoint that it is the skeleton of cement particles surrounded by $C-S-H$ gel which is critical to the realization of set, we can also study the effect of the initial dispersion of cement particles on the amount of hydration required for set. The amount of dispersion can also be modified experimentally by the use of superplasticizers or other additives [29]. To achieve dispersion in the model, we modify our cement particle placement conditions to ensure that every pair of particles is separated by at least a one pixel ($1\mu m$) distance, thus simulating the effect of a dispersive agent. Figure 9 shows the results obtained for a variety of systems of differing w/c ratios and particle size distributions. In every case, we find that the initial dispersion of the cement particles results in more hydration being required (i.e. a larger volume of $C_3S + C-S-H$) to bridge the gaps between particles and to achieve set. These results are in agreement with recently reported experiments [29].

Figure 9: *Set Point vs. W/C Ratio and Dispersion*

4.3 Percolation Transition *vs.* Shear Wave Onset

A plot of shear wave energy obtained from ultrasonic experiments on a set of cement slurries is provided in Figure 10, from [19]. This Figure shows a sharp onset, where significant shear wave energy is first transmitted, which we interpret as the point at which a continuous solid backbone first exists, as liquids cannot sustain a shear sound wave in the small frequency limit. After this initial onset, the amount of energy transmitted rises sharply as the connected backbone quickly assimilates the remaining isolated solid clusters. There is some experimental noise in the steeply ascending part of this plot, which may or may not have a microstructural origin. When all solids are part of the connected backbone, the shear modulus will then continue rising more gradually as the porosity continues to decrease with hydration. The similarity of the solids percolation plot in Figure 7 to the shear wave plot in Figure 10 is striking. This agreement is further evidence that the percolation arguments suggested by the model are the correct explanation of the shear wave data.

Figure 10: *Shear Wave Plot*

5 Discussion

The cellular automaton based approach provides a simple and powerful means of simulating the diverse physical and chemical processes that are involved in the hydration of cement slurries. The CA approach is justified by the fact that *any* tractable model of the process of cement hydration will be a simplification of the real activity. The approach allows a useful model to be developed despite the fact that much of the complex detail of cement hydration is not fully understood. It can also serve as a guide to suggest experimental work which may help to elucidate the key factors controlling cement hydration, such as the ultrasonic shear wave measurements which pinpoint the percolation point [19]. The lattice-based structure associated with a cellular automaton provides several opportunities for defining the initial state of the system, and for computing time-dependent properties of the model. A combination of 3D white noise based images and 2D micrograph starting images may be able to produce a realistic 3D starting image. Other effects, such as varying temperature, could be simulated by varying reaction probabilities in accordance with the Arrhenius law.

An additional advantage of cellular-automata-based microstructure models is the visualization capabilities which they afford. When the models are executed on a graphics workstation, the hydration can be viewed as it occurs. In addition to being a great aid in modifying code, the visualization provides further insight into how cement microstructure develops. In fact, personal computer versions of this CA cement model are now being utilized at a number of universities for undergraduate and graduate level classes in order to visually demonstrate the principles of cement hydration to students.

We are hoping to parallelize the present CA model so that much larger 3D lattices can be used. Some work has already been done on a parallel implementation of the original 2D algorithm onto a large parallel SIMD machine, the Connection Machine 2 (CM2), and onto a small 4 processor MIMD machine (a Silicon Graphics Iris) [16]. The CM2 appears to be ideally suited for running CA computations: it has achieved 10^8 site updates per second for a microcode implementation of a lattice gas CA - this would allow a cube of about $500 \times 500 \times 500$ sites to be updated every second [11]. Implementing the collision reactions for the cement CA model on a SIMD architecture was found to require sequential steps which reduced effective processor usage and a rate of only 10^5 site updates per second was attained. Implementation on a more massively parallel MIMD machine would allow a larger model incorporating finer detail and faster simulation runs. A cement hydration model of size $500 \times 500 \times 500$ updated every second would be desirable in order to represent the microstructure at an adequate level of detail and to permit a reasonable picture of the time evolution of the model to emerge.

Should such a model eventually be used to predict setting and/or thickening times for a given cement, it would, of course, be desirable that the execution of the model be faster than the real time taken by the cement to set. A concept of relevance to the present simulation work is algorithmic compressibility [15]. This notion is concerned with the extent to which physical processes may be simplified mathematically or, equivalently, compressed into algorithms from which the phenomena in question can be computed rapidly. A process which is algorithmically incompressible is one for which there is no predictability: the most efficient simulation of the process is the physical process itself. While it has been clearly demonstrated that the long term properties of cement paste can be predicted accurately in just a few hours of computer time, there may still be some question as to whether the algorithmic compression obtainable using these models is sufficient for short term properties such as set point. If even the fastest simulation takes as long as the real process, then we have gained limited genuine predictability, even if our understanding of what is occurring has been enhanced. There is, however, a range of evidence now available which suggests that at least some aspects of the behaviour of these systems is "universal" [35] and that therefore there is hope that it is possible to compress the behaviour in more elaborate simulations of the kind described in the present paper.

To make detailed comparisons with the time scales for dynamical evolution in real cements, it will be necessary to scale the time steps within the CA model appropriately. It may even prove possible to make comparisons with experimental heat evolution curves, determined by calorimetry, if an algorithm is included which computes the number of reactions which occur (i.e. the number of changes of species equals the number of sites at which a particular rule is applied), and assigns a specified heat release to each. This in turn could be fed back into temperature-dependent reaction probabilities (mentioned above) and a lattice-based algorithm that can be used for computing heat conduction [23], hence allowing for the effects of self-heating on the overall rate of hydration.

In conclusion, there are many additions, extensions and elaborations that could be made to the CA-type models discussed here without much difficulty. Such developments would serve to enhance the realism of an approach and models which we believe to be of considerable value in helping to unravel the complexity of cementitious materials.

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(purple = C_3S, blue = $ETR*$, green = $GYP*$, yellow = ETR, pink = C_3A)

Figure 11: *Ettringite needles - simulated*

Figure 12: *3D Particles generated from smoothed white noise (size* $64 \times 64 \times 64$*)*

(red = C_3S, purple = C_3A, green = GYP)

Figure 13: *3D Particles generated from smoothed white noise - multi-phase (size* $128 \times 128 \times 64$*)*

Figure 14: *BE image*

Figure 15: *X-Ray images*

(red = C_3S, magenta = C_2S, green = C_3A, orange = C_4AF, tan = gypsum)

Figure 16: *Composite image with w/c=0.672*

(yellow = $C-S-H$, light blue = FH_3, dark blue = CH)

Figure 17: *Microstructure: Hydration = 30%*

(yellow = $C-S-H$, light blue = FH_3, dark blue = CH)

Figure 18: *Microstructure: Hydration = 76%*