Experimental techniques for cement hydration studies

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ABSTRACT. Cement hydration kinetics is a complex problem involving dissolution, nucleation and growth and is still not well understood, particularly in a quantitative way. While cement systems are unique in certain aspects, they are also comparable to natural mineral systems. Therefore, geochemistry and particularly the study of mineral dissolution and growth may be able to provide insight and methods that can be utilized in cement hydration research. Here, we review mainly what is not known or what is currently used and applied in a problematic way. Examples are the typical Avrami approach, the application of Transition State Theory (TST) to overall reaction kinetics and the problem of reactive surface area. Finally, we suggest an integrated approach that combines vertical scanning interferometry (VSI) with other sophisticated analytical techniques such as atomic force microscopy (AFM) and theoretical model calculations based on a stochastic treatment.

Key words: Kinetics, Monte Carlo, cement, interferometry, dissolution.

INTRODUCTION

"*Cement sets when mixed with water by way of a complex series of chemical reactions still only partly understood.*" This statement in WIKIPEDIA (2010) describes a dilemma we are facing with the worlds most abundant building material. Cement hydration kinetics is a complex problem of dissolution, nucleation and growth that is still not well understood, particularly in a quantitative way. Thus, this paper is not focused on a review of what we already know but on what we do not know, and how we can potentially achieve a better understanding by introducing new experimental/analytical techniques into the mix of existing methods. The rate of cement hydration, particularly during the first 24 hours, is the complex interplay of many chemical reactions and a vast number of basic processes and elementary reactions (compare Lasaga and Luttge, 2004a, 2004b, for an in-depth discussion of basic processes versus elementary reactions). The overall kinetics of cement hydration involves the dissolution of several solid reactant phases, *e.g.*, alite (an impure form of tricalcium silicate, C_3S[1]), C_3A and gypsum (CSH_2), and the nucleation and growth of new phases, *e.g.*, calcium silicate hydrate (C-S-H), and ettringite.

It is an important goal of the cement industry to control the setting of cement and its resultant properties and those of its end product, concrete. To achieve this goal, chemical additives are applied to reduce or increase (accelerate or retard) the setting rates and influence the strength and other properties of concrete. However, when these additives are applied merely on an empirical basis, *i.e.*, by trial and error, the results are often unpredictable and inadequate. We are often unable to precisely enough predict the setting behavior of the cement, *i.e.*, the kinetics of nucleation and growth during (early) hydration, to achieve acceptable field performance of concrete. Similarly, it is also challenging to make predictions in a reproducible manner. Therefore, industry and academic researchers have focused on developing quantitative approaches for describing and modeling cement hydration and setting kinetics.

A comprehensive overview of achievements and obstacles in the path to developing a comprehensive description of cement hydration along with detailed experimental and analytical results was presented and discussed during a recent summit in Quebec City, Canada (Biernacki and Hanson, 2009). The discussion focused in part on successful and well established analytical technologies such as thermogravimetric analysis (TGA), the Vicat method, ultrasonic measurements, X-ray diffraction (XRD), and scanning electron microscopy (SEM), some of which have been described elsewhere (*e.g.*, Bullard et al., 2011, in press). There was also an interest in new experimental and analytical techniques, such as broadband time-domain-reflectometry dielectric spectroscopy (*e.g.*, Hager and Domszy, 2004), nuclear resonance reaction analysis (NRRA) (*e.g.*, Schweitzer et al., 2004; Schweitzer et al., 2005), and vertical scanning interferometry (VSI) (*e.g.*, Luttge et al., 1999). During this discussion, it quickly became clear that while there has been success from research based on both experimental techniques and modeling efforts, approaches based solely on bulk kinetics and overall reaction rates have significant constraints and limitations.

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[1] Using the cement chemistry notation and mineral names
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What seems necessary is a fundamental and quantitative understanding of the complex processes that govern cement hydration kinetics and their interplay. Some assistance may come from an outside but related field, *i.e.*, low-temperature aqueous geochemistry. Geochemists have struggled with similar problems such as mineral weathering in soils, stability of nuclear waste deposits, and acid mine drainage including mineral reactions in mine tailings (Blum and Lasaga, 1987; White and Brantley, 1995, Arvidson et al., 2003; Asta et al., 2010; Gherbi et al., 2010). In these systems, primary minerals such as (alumino-) silicates, carbonates and others dissolve and new so-called secondary minerals such as clays are precipitated. Many of these mineral dissolution and growth reactions have been studied intensively over the last few decades (Gautier et al., 1994; Schott and Oelkers, 1995; White and Brantley, 1995; Oelkers, 2001; Berger et al., 1994, 2002; Morse et al., 2007; Luttge and Arvidson, 2008) and a number of experimental, analytical and theoretical tools and strategies (Luttge et al., 1999; Luttge and Arvidson, 2008; Parker et al., 2001; Higgins et al., 1998, 2002; Meakin and Rosso, 2008) have been developed to generate a quantitative understanding. Some of the methods and strategies may be well suited for application in the field of cement hydration kinetics as well.

In this paper, an approach that utilizes vertical scanning interferometry (VSI) together with X-ray diffraction techniques, atomic force microscopy (AFM), electron microscopy techniques (SEM, TEM), confocal and fluorescence microscopy and X-ray Photoelectron Spectroscopy (XPS) will be proposed. Luttge (2004) and Luttge and Arvidson (2008) have argued that these sophisticated analytical and experimental techniques are particularly powerful when combined with modeling efforts based on parameterized kinetic Monte Carlo simulations (Lasaga and Luttge, 2001, 2003, 2004a; Zhang and Luttge, 2007, 2008, 2009a, 2009b; Cama et al., 2010). Below, we will outline and review a general approach that was developed in a similar way for geochemical questions. We will discuss a few critical questions that may be central for cement systems as well, and highlight some key methods that could serve – among others – as cornerstones of a new approach for the complex and important systems associated with portland cement.

A BASIC CONCEPT FOR THE KINETIC TREATMENT

Bulk versus microscopic techniques

There are a number of similar problems and challenges that investigators of both cement and mineral weathering systems have to tackle. In the past, when instruments such as atomic force microscopes (AFM), vertical scanning interferometers (VSI), and X-ray photoelectron spectrometers (XPS) were not available for direct investigations of the water-mineral interface, geochemists focused their experimental and analytical approaches mainly on solution chemistry, pH, and the changes of saturation state during a dissolution reaction. Typical reaction rates of many geological and environmentally important minerals like alumino-silicates at low, *i.e.*, earth surface, temperatures, are on the order of 10^{-14} to 10^{-16} moles/m^2/s (*e.g.*, Lasaga, 1998 and see also review in Blum and Stillings, 1995). This fact forced experimentalists to conduct their studies with mineral

powders to increase the surface area of the solids and to choose far-from-equilibrium conditions to achieve rates that could be quantified (see discussion in, *e.g.*, White, 1995 and Ganor et al., 2005). Note that this situation is very comparable to the typical conditions in early cement hydration where extremely fine mineral powders react. As a result of their effort, geochemists have created a large pool of reliable, internally consistent data for minerals and synthetic crystalline materials. However, the detailed kinetic interpretation of these data with respect to reaction mechanism(s) is usually difficult and ambiguous, leading to various interpretations and so-called "rate laws". For example, Berger et al. (2002) elucidate this dilemma in their brief review (see also discussion below). In addition, estimated dissolution rates (*e.g.*, Erel et al., 2004; Ganor et al., 2005) in natural systems indicate that the laboratory data can be utilized only if one is able to identify the function of Gibbs free energy (ΔG) that is suitable for a reliable extrapolation of the far-from-equilibrium data set to conditions much closer to equilibrium.

Most importantly, it is the complexity of the system at hand, and the fact that the reaction processes may be observed and measured at several different time and length scales (Fig. 1), that complicates matters and our ability to predict the reaction kinetics correctly.
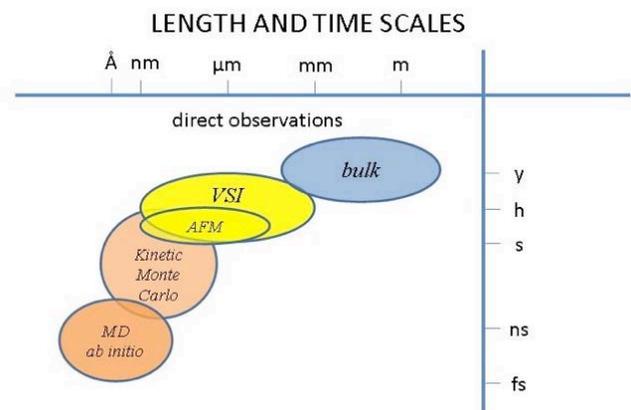

Fig. 1. *Lengths and time scales of various analytical, experimental and modeling techniques used in the study of reaction kinetics.*

A critical impediment for substantial progress is that results obtained at a certain time and length scale are often not connected easily with results obtained at a different scale. For example, it is possible to measure the dissolution rate of solid materials such as crystals or glass by measuring the weight loss and/or volume loss. Experimentally, bulk dissolution rates, *Rate*, are often measured as the change of a certain concentration, dc, with changing time, dt. This bulk rate can be determined as a function of, *e.g.*, temperature, T, pH, saturation state of the solution, and difference in Gibbs free energy, ΔG, between the crystal and the fluid in contact with the solid's surface. Equation (1) describes this approach and can be found in various forms in the literature, *e.g.*:

$$Rate = \mathrm{d}c_i/\mathrm{d}t = k \, A \, f(\Delta G) \qquad (1)$$

where k is the rate constant or intrinsic rate in units of [mol m^{-2} s^{-1}], A is the surface area of the solid in contact with the fluid and $f(\Delta G)$ is some function of the Gibbs free energy. Ignoring the more complex problem of crystal nucleation, it

is also possible to write a similar equation for the crystal growth process:

$$Rate = dc_i/dt = k\,A\,(c_{i,eq} - c_i)^n \qquad (2)$$

where $c_{i,eq}$ is the equilibrium concentration of species i, and c_i is the actual concentration of species i at time t. The dissolution and growth processes are in fact not independent but coupled by the saturation state of the fluid phase. Luttge and Metz (1991) have shown an example of a possible theoretical treatment for such coupled dissolution-growth kinetics. This treatment requires solving a set of simultaneous differential equations. The system of differential equations is complete if it describes the behavior of all relevant chemical species with equations of the type:

$$dc_i/dt = [k_{diss}\,A_{diss}\,(1- (c_{i,eq}c_i)/L_{diss})] + [k_{growth}\,A_{growth}\,(1-(c_{i,eq}c_i)/L_{growth})] \qquad (3)$$

Luttge and Metz demonstrate in their discussion that it is impossible to define a single rate limiting step such as the dissolution of a specific reactant. It is much more likely that the rate limiting process will change in the course of the overall reaction process. If we consider now our toolbox of experimental and analytical methods then it seems fair to say that none of the current techniques that focus on overall reaction rates by measuring fluid composition can be used to derive conclusions about the actual microscopic dissolution or growth mechanisms. Note that this statement is in sharp contrast to many attempts made in the past (compare, *e.g.*, Oelkers, 2001). A key problem is the determination of the so-called activation energy. This problem is not solved by re-naming the energy term as "apparent" activation energy. It is important to note that the activation energy is an integral part of the transition state theory (TST; Eyring, 1938). TST is valid provided it is applied to the kinetics of *elementary reactions*; however, it cannot be applied successfully to overall crystal dissolution and growth reactions. Lasaga and Luttge (2004a, 2004b) and Luttge (2005) have discussed the issue in detail, and we will give a brief summary, below.

Before we discuss the TST concept in more detail, we return to the problem of scale. The movement and development of surface features such as etch pits, hillocks, and steps can be conventionally measured by using atomic force (AFM) and scanning force microscopy (SFM) methods. These sophisticated techniques can precisely quantify in situ rates of changing surface features during the actual dissolution and growth process. The high spatial resolution that these systems provide (about 50 pm, Asylum Research) allows the measurement of step velocities with unprecedented precision. However, while it is theoretically possible to link, for example, step velocities with bulk rates, it has proven difficult in "real" systems to achieve consistent results. Vinson and Luttge (2005) have discussed this topic in detail for the dissolution of calcite crystals.

Activation energies and Transition State Theory (TST)

Historically, overall dissolution and precipitation kinetics have been quantified as bulk reaction kinetics and so-called "activation energies" have been derived from Avrami-type approaches. Lasaga and Luttge, and others have discussed the limitations of such approaches for overall mineral dissolution reactions and similar conclusions can be drawn for cement systems. Here, we want to review briefly this discussion about the applicability of TST to the problem of crystal dissolution (compare for a detailed discussion Lasaga and Luttge, 2004b; Luttge, 2005).

TST-based rate laws are routinely used to fit experimental rate data, both in geochemical and more recently by Bullard for cement reactions (see Bullard, 2008). However, Lasaga and Luttge have argued that transition state theory (Eyring, 1935a, 1935b) should not be applied to overall dissolution reactions (*e.g.*, Lasaga and Luttge, 2004a, 2004b, 2005). Here, we highlight briefly the main arguments that they used to show that TST-based rate laws are insufficient to explain crystal dissolution kinetics as a function of distance from equilibrium. First let us review the common approach. This discussion is important, because the quantitative understanding and treatment of cement hydration systems need the dependence of the dissolution rate of primary minerals and other substances as a function of distance from equilibrium, *i.e.*, as a function of the difference in Gibbs free energy (ΔG). Currently, many models simply use a dependence of the rate on ΔG given by a rate law such as:

$$Rate = A\,(1 - e\alpha\Delta G/RT) \qquad (4)$$

where A is a coefficient that is supposedly "stoichiometric" and related to the reaction controlling the overall rate of the complex global observed reaction (*e.g.*, Lasaga and Luttge, 2004b). It is problematic that Eq. (4) is not derived from a detailed model of the dissolution process incorporating the crystal lattice. Instead, a rate determining "precursor" surface complex is typically postulated (*e.g.*, Oelkers, 2001). It is then assumed that the rate of the overall dissolution reaction depends on just this particular reaction (*e.g.*, Helgeson, 1971; Lichtner et al., 1996). It is further assumed that this rate is proportional to the concentration of the surface complex, and implicitly that lattice dislocations have no effect on the reaction rate. However, we know that this is not the case (*e.g.*, Eyring, 1935a, p. 189). The pure focus on precursors as rate determinants implies that glass would dissolve with the same rate as crystalline matter of the same chemical composition at the same conditions (compare, *e.g.*, Oelkers, 2001). Such a result is highly unlikely as discussed by, *e.g.*, Lasaga and Luttge (2004a, 2004b, 2005; Zhang and Luttge, 2007). In contrast, their stepwave model treats crystal dissolution as stochastic processes and incorporates the crystal lattice. An additional argument was presented by Icenhower et al. (2004) who found significant deviation from TST even for glass dissolution. Another prerequisite for the use of Eq. (4) is the assumption that the *same* surface complex controls also the crystal growth process. Finally, this reaction must be defined as an *elementary* reaction or a chain of elementary reactions (*e.g.*, Boudart, 1976; White and Brantley, 1995) because activated complexes are specific to a particular elementary reaction (*e.g.*, Laidler, 1987; Lasaga, 1998). This list shows that the real dispute does not arise from TST but from the questions if (i) a simple surface adsorption model that uses TST is sufficient to describe the kinetics of complex crystal dissolution; and (ii) how the energy difference ΔE of a rate-limiting elementary reaction relates to the overall dissolution rate (see Lasaga and Luttge, 2004a for a detailed discussion). Here, we want to state only

that while the ratio of the rate constants of elementary reactions obeys the TST relation (5):

$$k^+ / k^- = \exp(\Delta E/kT) , \qquad (5)$$

the activation energy for the overall reaction, E_{act}, does not reflect the activation energy needed to break the individual bond, $E\ddagger$, but the number of bonds, n, and the energy difference between an original bond and a broken bond, ΔE, i.e.:

$$E_{act} = n \, \Delta E \qquad (6)$$

where ΔE is the energy difference between the intact bond and broken bond states, k the Boltzmann's constant, and T is temperature in (K). Lasaga 1998 (p. 190), Polany (1992), and others have explained in detail that the overall activation energy is not necessarily the same as the activation energy of a single elementary process, nor is it the same as the activation energy of a single rate limiting step. Therefore, Eq. (6) does not contain $E\ddagger$ but ΔE. Similar considerations have been applied successfully to crystal growth kinetics (Gilmer, 1976, 1977, 1980; Wehrli, 1989a, 1989b; see also Blum and Lasaga, 1987).

The frequent and incorrect application of TST in combination with surface adsorption models to overall crystal dissolution reactions can be explained only if Eq. (6) and its implications have not been recognized. The assumption of a precursor surface complex, often interpreted as the activated complex in the sense of TST, is problematic in itself. However, even if this scenario would exist we just saw that Eq. (6) does not contain the energy term, $E\ddagger$, of the transition state itself and therefore, the activation energy of a crystal dissolution reaction as measured by practical means in the laboratory most likely does not reflect the activation

energy for the breaking of one particular bond or a suite of bonds (Lasaga and Luttge, 2004a, 2004b, 2005).

One argument, however, that is often made seems to counter this assessment on first glance: "the experimental rate data support TST based rate laws". Lasaga and Luttge have discussed this apparent dilemma. Here, we summarize their main arguments. (i) As discussed above, TST can be applied only to an elementary reaction for which a unique, i.e., mathematically well-defined transition state can be identified (e.g., a stationary point on the adiabatic multidimensional potential energy surface involving reactants and products with a unique negative eigenvalue in both positive and negative directions). (ii) TST allows a relation between the forward and reverse rate constants but only of an elementary reaction. (iii) To connect this reaction mechanism to any other overall reaction requires the derivation of a relation involving the distance from equilibrium, i.e., ΔG. This derivation should come from the standard kinetic treatment of the full reaction mechanism. It is not justified, per se, to assume that it would be the same as for a single elementary reaction and "prove" it by fitting experimental data to such a function.

This is a central challenge of chemical kinetics because under most circumstances it is simply not possible to collect data that are sufficiently precise such that they uniquely define a given reaction mechanism. Several authors have focused on the experimental determination of rate data for important minerals as a function of solution composition (Gautier et al., 1994; Oelkers et al., 1994; Devidal et al., 1997; Berger et al., 2002). All of them apply TST-based rate laws to fit their data. As an example, Lasaga and Luttge (2004b) have analyzed the data of Gautier et al. (1994) (see Figs. 2a-c) on dissolution of K-feldspar to critically explore what kinetic information may be extracted.
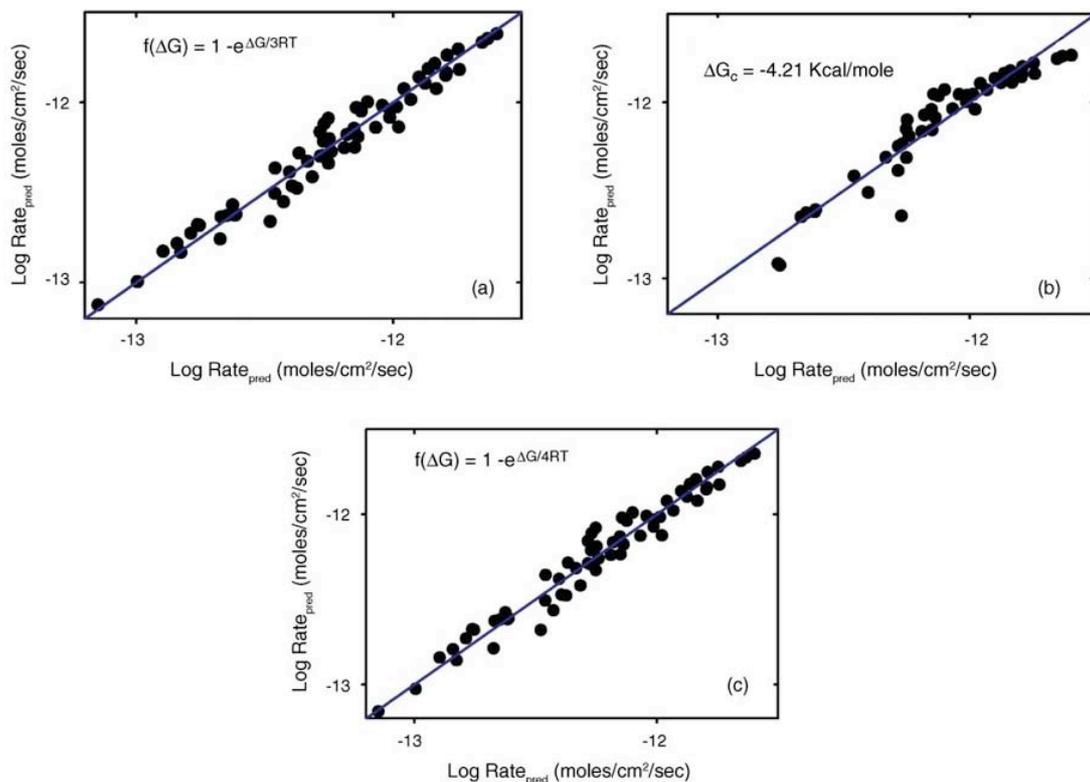

Fig. 2. *Lasaga and Luttge's (2004b) comparison of predicted and observed data for a variety of kinetic models using the K-feldspar dissolution data of Gautier et al. (1994): (a) TST-like ΔG dependence multiplied by a power law in Si and Al. ΔG is defined as in Luttge et al. (1999); $f(\Delta G) \equiv 1 - e^{\Delta G /3RT}$; (b) etch pit-based dissolution stepwave model (Lasaga and Luttge, 2001) multiplied by a power law in Si and Al; (c) same as (a) but using the atomic based ΔG definition.*

This analysis revealed that the measured rate data cannot be used to distinguish between three different kinetic models. The kinetic models were significantly different from each other, *i.e.*, (i) a simple transition state formulation of the ΔG dependence; (ii) a model grounded in the statistical theory of crystal growth and dissolution (Lasaga and Luttge, 2004a); and (iii) a transition state formulation of the ΔG dependence with the factor of 4 in the TST term (see Figs 2a-c). This demonstration clarifies that mathematical fitting of experimental dissolution data alone cannot be used to identify reaction mechanisms. While Lasaga and Luttge focused exclusively on geochemical examples, the main conclusions apply in an analogous way to cement systems as well. Before we introduce an alternative approach we will review another challenge to quantitative measurements of crystal dissolution and growth kinetics.

The surface area problem has been discussed intensively over the last two decades. The measurement of surface area is critical for kinetic studies and rate determination for solid-fluid systems that are surface-controlled. This is a central and as yet unsolved problem, because reaction rate scales with surface area, and thus a solution is not in sight in the foreseeable future. Thus, the question remains how to "correctly" quantify the surface area involved in crystal-fluid interactions (*e.g.*, Gautier et al., 1994; Hochella and Banfield, 1995; Jeschke and Dreybrodt, 2002; Ganor et al., 2005)? This question leads quickly into a more general problem of quantification of surface area, *reactive* versus *total* surface area and their definitions. Luttge (2004, 2005) and particularly Luttge and Arvidson (2008), among others, have discussed the problem in detail. Currently, the only reliable and quantitative measurement of surface area of fine powders is the so-called BET method (Brunauer et al., 1938). However, there is a general consensus that the surface area relevant to reaction rate measurements should be considered a function of time. This leads to a modification of equation (1):

$$RATE = k \cdot A(t) \cdot f(\Delta G),   (7)$$

where $A(t)$ represents the time dependent changes of total or BET surface area that participates in the fluid-solid interaction. However, although we may be able to measure the initial and final surface areas, we cannot measure its change as a function of time. In addition, we face the problem that surface area is not homogeneously reactive, as indicated by the formation of etch pits. Currently, there is no good strategy to measure this so-called reactive surface area, and it is certainly not correct to simply express the "reactive" surface-area term as a geometric unit, *e.g.*, [m^2]. Lastly, the use of the term *reactive* area implies that the remaining area is *nonreactive*, an implication that is neither useful nor accurate. Instead, it might be much more useful to introduce a "reactivity" term that incorporates all energetic sites at the surface of interest and their potential contribution to the overall dissolution process (Luttge, 2005). As a consequence, we usually have to agree that the quantification of surface area poses the largest uncertainty in the determination of reaction rate constants because all reaction rates must be normalized by surface area. In geochemical problems this uncertainty can be several orders of magnitude.

The discussion of the surface area problem has largely overshadowed another question, *i.e.*, the relationship of dissolution rate and Gibbs free energy, ΔG. Note that some authors prefer to use reaction affinity, A, (De Donder, 1927) instead of ΔG (*e.g.*, Berger et al., 1994, 2002; Gautier et al., 1994; Schott and Oelkers, 1995; Oelkers, 2001). Luttge (2005) pointed out that this emphasis on reaction affinity has lead to some confusion. The difference, however, between the two variables is of minor importance[2]. Thermo-dynamically, both parameters are clearly defined and related by the equation:

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{P,T}   (8a)$$

where ξ is the extent or progress of reaction. Thus at constant temperature and pressure:

$$dG = \sum_i \mu_i dn_i = Ad\xi   (8b)$$

Equation 8b shows that mathematically, the Gibbs free energy and affinity are related by a simple change of variables. Of more serious consequence is our ability or inability to measure the dependence of dissolution and growth rates on ΔG. Only if this dependence is quantifiable are we in a position to predict kinetic behavior and absolute reaction rates. While the ΔG-dependence for the growth process is typically quite well understood, the dependence for the dissolution process is not. Recently, several research groups have discussed this problem in more detail (*e.g.*, Luttge, 2005; Hellmann and Tisserand, 2006; Hellmann et al., 2009; Arvidson and Luttge, 2010; Daval et al., 2010). It is particularly difficult to predict the behavior at close-to-equilibrium conditions because it is experimentally almost impossible (or at least very difficult) to obtain reliable rate data. Some success, however, was reported by Beig and Luttge (2006) and more recently by Arvidson and Luttge (2010) by utilizing vertical scanning interferometry (VSI) techniques. We will discuss this technique further below.

An Integrated Approach Using VSI and kinetic Monte Carlo Simulations

Interferometry techniques have a strong potential to become transformational technologies in several different fields such as biomedicine, geomicrobiology, geochemistry, corrosion engineering, and material science. In the following section we will introduce the VSI technique and demonstrate its use for the field of cement research, particularly for the quantification of cement setting kinetics. It is also important to note that both data acquisition rates of AFM and VSI instruments are too slow to permit the study of kinetic processes at the atomic or molecular scale, even if the necessary spatial resolution was available. Therefore, we have complemented our experimental approach with kinetic Monte Carlo (kMC) calculations (for a more detailed discussion see Thomas et al., 2011, in press). kMC treats crystal dissolution as a stochastic, many-body problem and allows the treatment of systems that are large enough to compare their computational results directly with AFM

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[2] van't Hoff (1886) already concluded that the real measure of chemical affinity is the change of Gibbs (or Helmholtz) free energy.

and VSI measurements. In this way computer calculations and laboratory experiments can be combined and create a feedback situation that produces surprisingly good results (*e.g.*, Fewless and Luttge, 2003, unpub.; Cama et al., 2010; Luttge and Arvidson, 2010).

It is important to emphasize that this approach abandons the limitations of closed-form equations and conventional "rate laws" and moves forward to a treatment of crystal reaction kinetics as a dynamic, many-body problem that must be solved stochastically. At the center of our model is a fundamental understanding of the kinetics at kink sites that govern the overall processes of both crystal dissolution and growth. The kink site has the central role in crystal growth and dissolution theory. The combination of two properties is the reason for this control, *i.e.*, the number of bonds that bind a molecule in kink site position is half the number of bonds that coordinate the equivalent molecule in the bulk lattice. Additionally, this site is self-replicating, *i.e.*, addition or removal of a molecule generates the same configuration. The change in concept and treatment brings with it important consequences, *i.e.*, it permits a more fundamental insight into the molecular surface processes and their cumulative result, including variation of rate within crystal systems, the effect of non-stoichiometric compositions, the relationship of ordering and temperature, and other related phenomena. These insights potentially lead to a comprehensive theory of crystal dissolution and a unified dissolution-growth theory. However, they also require conceptual revisions in our approach to problems involving crystal-fluid interactions and an analytical method that is capable of measuring cumulative changes at crystal surfaces quickly and precisely. Vertical scanning interferometry offers this capability, and we discuss this method, its capabilities, and applications in more detail in the following section.

Vertical Scanning Interferometry (VSI) and the closely related technique, *i.e.*, *phase shifting interferometry* (PSI) are light optical, minimally invasive and non-destructive techniques that can be used to study surface topography and the processes that alter surfaces. VSI develops its full strength as complementary technique to atomic force, confocal and fluorescence microscopy, and scanning force techniques (AFM and SFM; for an in depth description of VSI see, *e.g.*, Luttge et al., 1999; Arvidson et al., 2003; Luttge et al., 2003; Arvidson et al., 2004; Luttge, 2005). Like AFM, VSI quantifies both surface topography and changes of surface topography during dissolution, corrosion, or nucleation and growth processes. Its main advantage is fast data acquisition, large field of view, with a scan range of 100 microns (this can be extended to the millimeter range), and great precision of measurement, with high vertical resolution that depends on the scan range but is typically better than 2 nanometers.

While we used various versions of ADE Phase Shift's MicroXAM MP8 for the bulk of our published studies, we began recently to utilize the ZEMAPPER (Zemetrics/ZYGO), a newly developed instrument with significantly improved performance. The vertical resolution of today's state-of-the-art commercially available instruments used for our published work is in the sub-angstrom to one-nanometer scale. The lateral

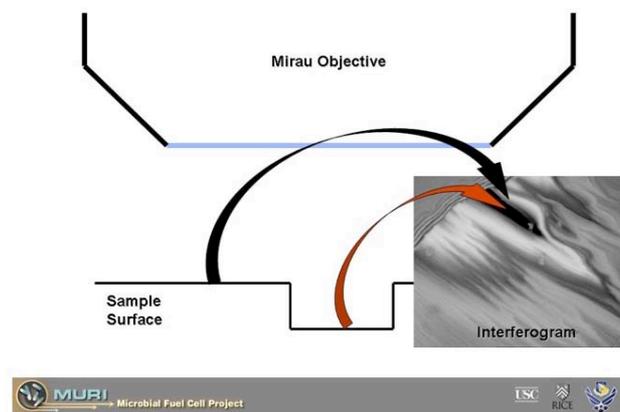resolution is a function of the particular Mirau objective used in the experiment (Fig. 3).

Fig. 3. *Sketch demonstrating a Mirau interferometric objective generating an interferogram.*

VSI provides a significantly larger field of view than AFM (up to one square millimeter per scan). Its fast scan speed (up to 14 microns per second) allows the acquisition of a large number of measurements that can be overlapped by, *e.g.*, 10%. In this case 400,000 data points would be identical in two overlapping data sets given that a 2k camera was used. Stitching techniques with subpixel registration allows a seamless welding of those measurements. We typically use a convergence analysis of well defined surface roughness parameters to indicate the size of the field of view required for a representative measurement of a given sample (Fischer et al., 2009). Using VSI, even living microorganisms and their interactions with solid substrate surfaces can be observed simultaneously (*e.g.*, Davis et al., 2007; Waters et al., 2008).

While VSI is mainly used for surface topography measurements, we have developed this technique for the quantification of dissolution, corrosion, and growth rates that alter the existing solid surface. Experience has led us to believe that almost any reflective surface can be measured, *e.g.*, minerals, glass, metals, ceramics, and even as already mentioned bacteria and biofilm on substrates. And, as illustrated in Figs. 4 and 5, it is possible to apply the technique to cement clinkers. For example, Luttge et al. (1999) and Arvidson and Luttge (2010) have described in detail how dissolution and growth rates can be quantified as overall rates or spatially resolved. These rate measurements are currently, and likely, the most precise way of determining solid fluid reaction rates. For convenience, we will summarize the process here, again.

The task requires a number of time-lapse observations that quantify the evolution of surface topography. It is a prerequisite to establish "fixed" spots at the reacting surface to obtain absolute reaction rates (see below). This problem is usually solved by physically masking several micron-sized areas of the original pristine surface. During the reaction and at the end of the experiments the masks can be removed and any part of the reacting surface can be measured with respect to the internal reference height. All rates determined with VSI are based on surface-normal retreat or advance velocities. An example is the change

in height, h, of a given point (i,j) on a solid surface, *e.g.*, a crystal face, during the time interval from t_1 to t_2:

$$\frac{\Delta h_{i,j}}{\Delta t} = \frac{h_{i,j2} - h_{i,j1}}{t_2 - t_1} \qquad (9)$$

$$= v_{i,j(hkl)}, \qquad (10)$$

where $v_{i,j\,(hkl)}$ is the velocity of dissolution, corrosion or growth of every i,j coordinate at the given surface in units of $[\text{m s}^{-1}]$. The rate constant, $k_{i,j}$, often called the intrinsic rate is then computed by dividing by the molar volume ($\overline{V}$) of the material dissolved or grown,

$$k_{i,j} = v_{(hkl)} \cdot \overline{V}^{-1}, \qquad (11)$$
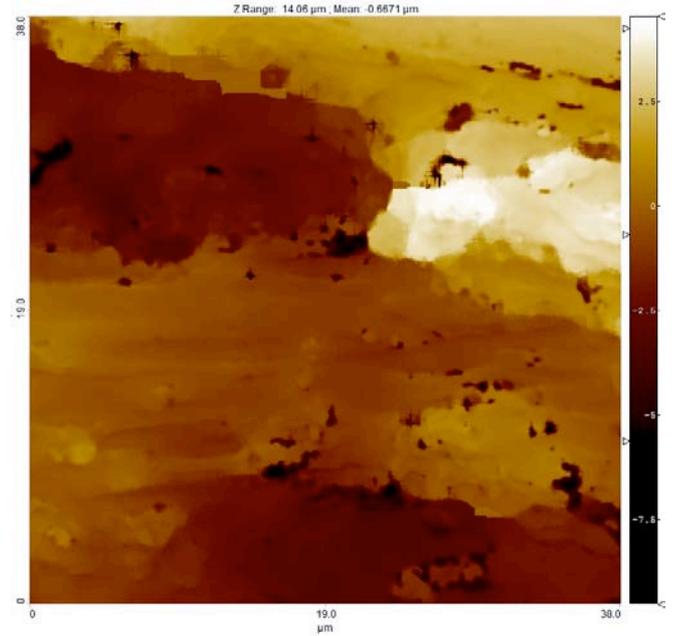
Fig. 4. *Color-coded VSI generated height map of a polished unreacted Portland clinker.*
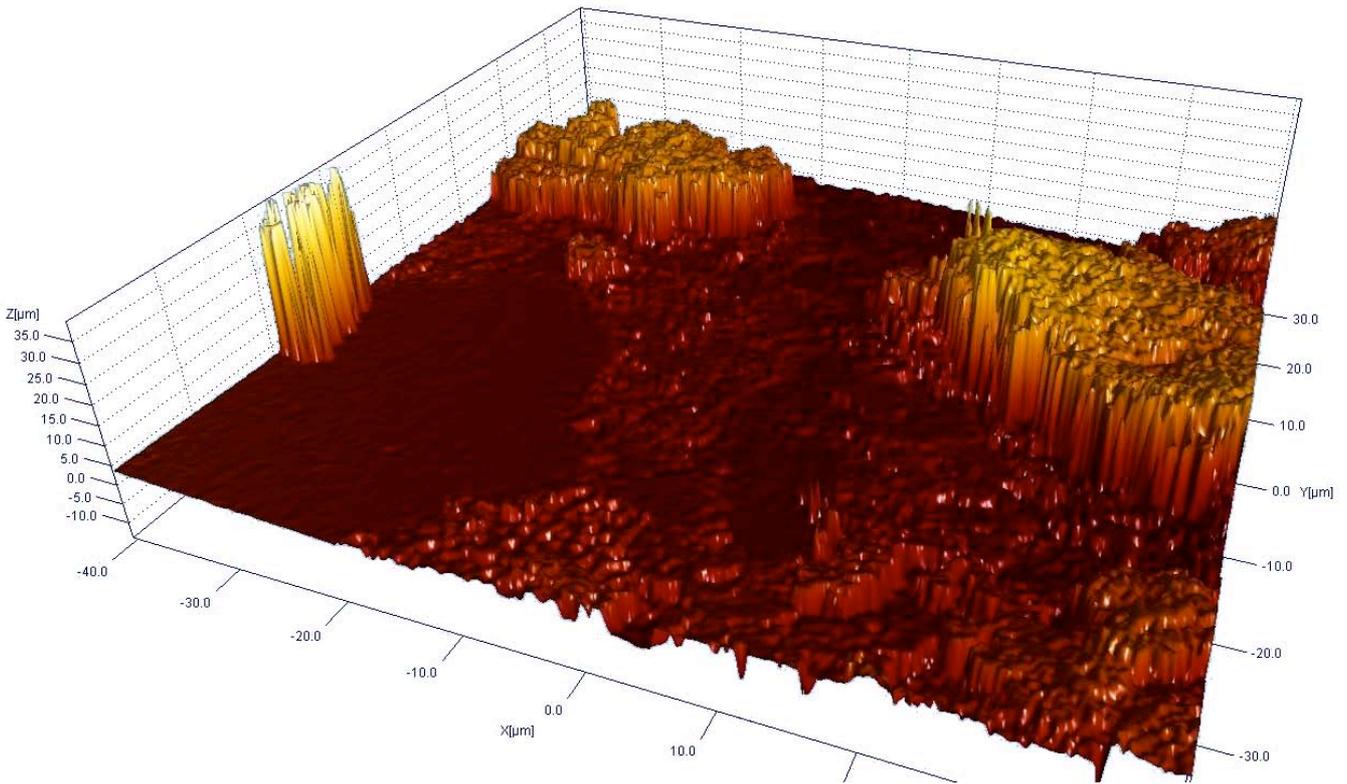
Fig. 5. *3-D visualization of a hydrated Portland clinker after about 3 days of reaction time. The two "islands" are newly formed cement phases while the original clinker phases, alite among others have begun their dissolution process.*

Rates computed in this way have units of flux $[\text{mol m}^{-2}\,\text{s}^{-1}]$. We can now either analyze all intrinsic rates, $k_{i,j}$, spatially resolved or sum them up and calculate an average rate: constant, k,:

$$k = \sum \frac{k_{i,j}}{N_{i,j}}, \qquad (12)$$

to obtain an intrinsic rate for the entire surface. $N_{i,j}$ is the number of all pixels, ij, measured in a VSI scan or in a sequence of stitched measurements.

By using a 4k camera, one scan provides up to 4,000,000 height data. From this treatment, we see that the rate constant is itself not a "true" constant but depends on the number and distribution of reactive sites across the surface. In case of a crystal surface the rate will depend critically on the number and distribution of kink sites (Luttge and Arvidson, 2010). This insight leads directly into the above-

mentioned statistical treatment of reaction rates on the crystal surface and provides a sound basis for the complementary use of parameterized kinetic Monte Carlo simulations (*e.g.*, Luttge, 2004; Zhang and Luttge, 2007, 2008; 2009a, 2009b; Cama et al., 2010).

With respect to cement systems VSI offers new exciting perspectives. Arvidson and Luttge (2010) have developed a reaction cell that allows studying the reaction directly. The sample material, *i.e.*, clinker, or actual cement particles, can be placed into this cell and water can be added in a well-controlled way, *i.e.*, pH, temperature, saturation state, and certain additives, and their effect on the reaction kinetics can be tested. The interferometer measures the response of, *e.g.*, a clinker sample. That means dissolution rates and pre-cipitation of cement phases can be observed and quantified. The samples do not require specific preparation such as coatings for electron microscopy applications. Figures 4 and 5 are typical examples obtained from a reacting portland cement clinker.

As a light optical technique VSI has limits imposed in part by the optical resolution of the system at a given wavelength. However, because of its 3-dimensional data acquisition, it is possible to utilize so-called super-resolution (SR) techniques. Arvidson and Luttge (2010) and Luttge (2003) have described this approach in detail. Here, we review this work briefly because SR-VSI may be a powerful approach in the field of cement research particularly if ordinary VSI systems are camera limited in their resolution. Super-resolution techniques may be useful also because of the often very small crystallites in the cement clinker and the small size of the newly formed cement phases.

Super-resolution VSI

In past applications of VSI technology to problems of fluid-surface interactions, it became evident that an improved lateral resolution of the instrument would be desirable for complex surfaces and very small particles and surface features. Also, it was our goal to improve the lateral resolution of VSI to develop a tool that is capable of directly connecting with the atomic force and scanning force microscope technologies. While the developers of the Zemapper have approached this task more recently through hardware solutions and the use of a shorter wavelength, *i.e.*, improved objectives, a high-resolution camera system, and the use of blue light instead of green light, we have achieved the goal by the application of *super-resolution* techniques, *i.e.*, a combination of multiple measurements of slightly offset frames and the application of deconvolution techniques (Fig. 6).

Figures 7-12 demonstrate our approach, *e.g.*, serial nano-positioning of the sample, and data reduction through image processing and deconvolution techniques. By making a number of design changes (described in Luttge, 2003) sample position and orientation can be independently controlled through a stack of computer-controlled nano-positioning stages (PI). As a result, the sample position can be controlled in 3-D space with a precision of ~1 nanometer or better. To achieve the gain in resolution, typically 4, 16, or 64 measurements are taken at offsets of fractions of a pixel, *i.e.*, one half, one quarter, and one-eighth pixel offsets, respectively. These measurements are subsequently interlaced to produce a new image that is blurred but contains more information. The interlaced image is then

treated with image processing techniques. That means Fourier-based, deconvolution operators are applied to remove the "blur", and transform the interlaced composite into a new image *at higher resolution*. This deconvolved image contains *new* information, not visible in any of the base frames (Figs. 9-12). The extent of resolution enhancement increases as the reciprocal of subpixel offset.
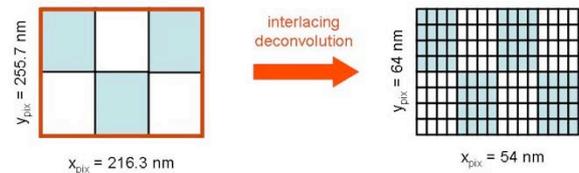

Fig. 6. *Schematic demonstration of the super-resolution technique that combines the interlacing of several measurements offset by subpixel distances and subsequent deconvolution into a de-blurred higher resolved image.*
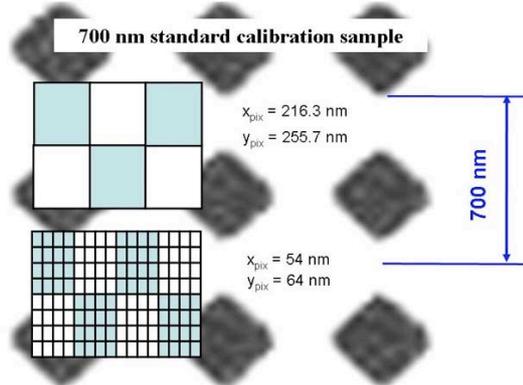

Fig. 7. *Schematic sketch showing a commercial, certified sample grid with a full period of 700 nm used in our feasibility study of a 4x super-resolution enhancement.*
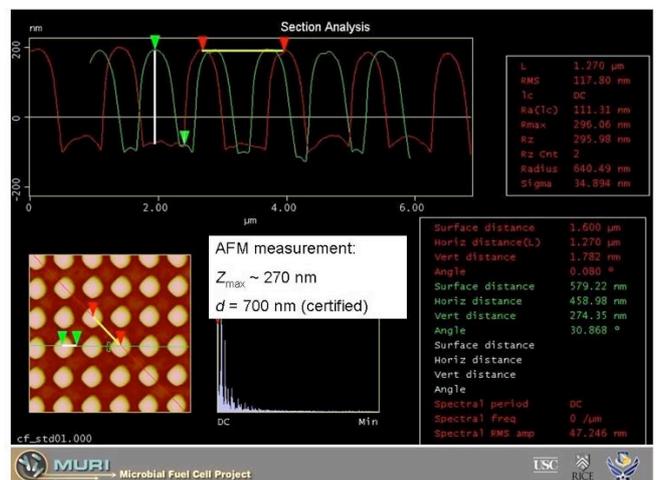

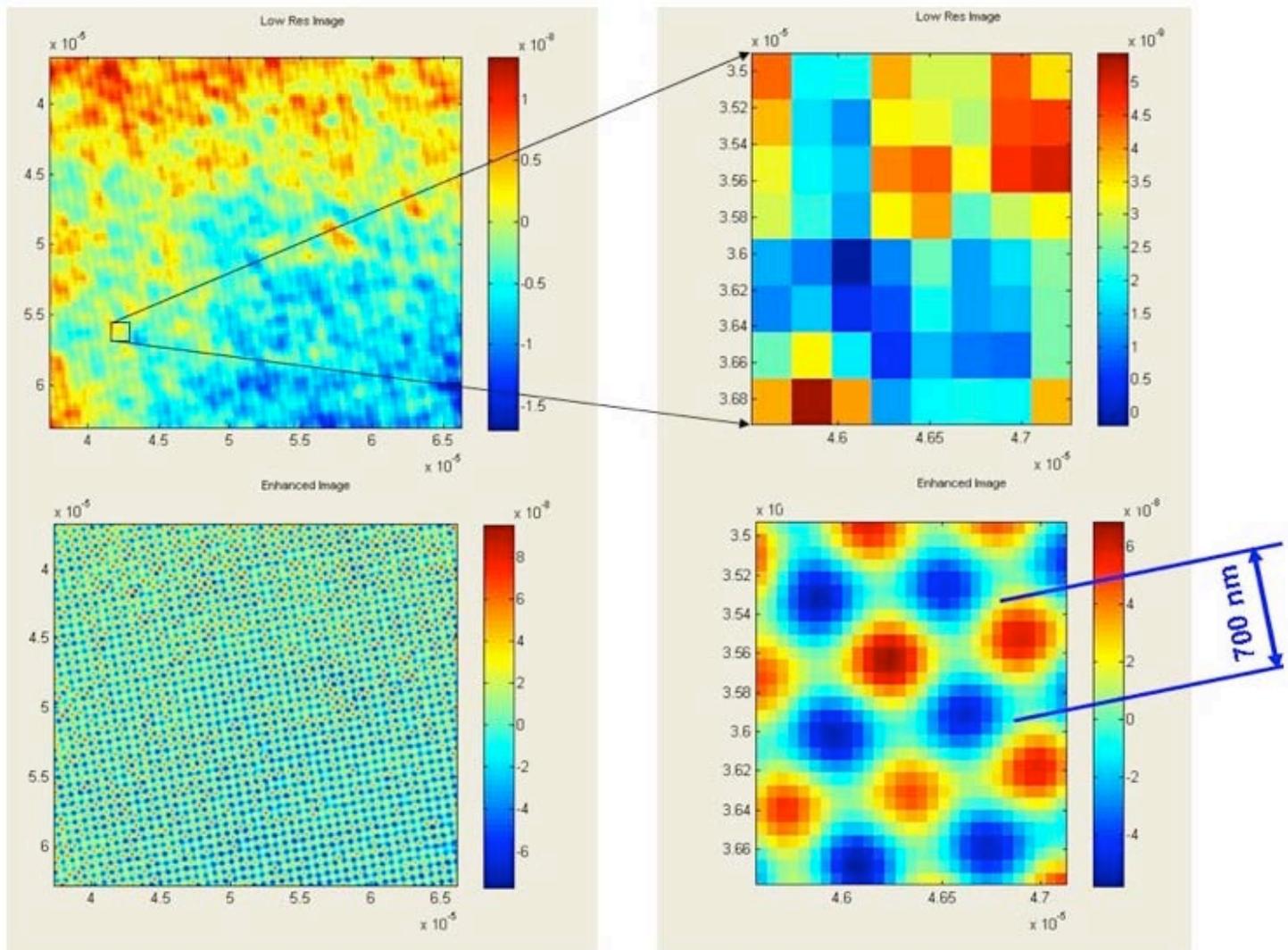**Fig. 8.** *Chart showing independent AFM measurement of the actual 700 nm sample grid.*

Fig. 9. *Color-coded height maps acquired with the MicroXAM (upper half of the figure) and 4x enhanced, deconvolved images generated from 16 measurements taken as described above (lower half of the figure). Note that the left hand height map represents about 30 microns in X and the right hand map represents about 4 microns length in X direction. Both data sets are subsets of the original measurements of 164 x 124 microns size.*
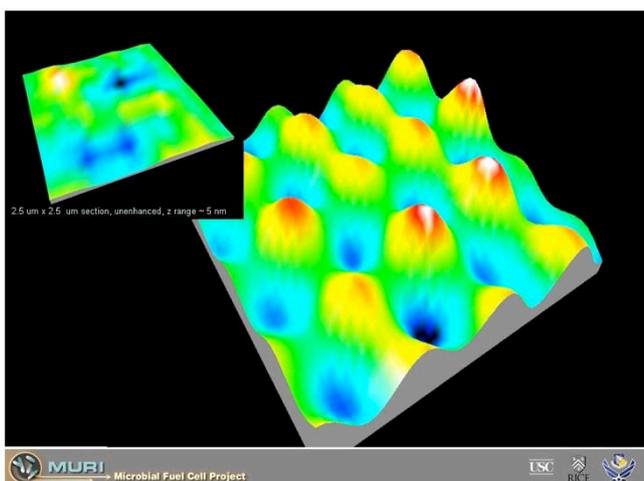

Fig. 10. *3-d visualization of the right hand color-coded height maps in Fig. 9.*

SUMMARY

In this manuscript we have discussed a variety of different topics, and it is most appropriate at this point to summarize the most important thoughts and draw a few conclusions. First, we understand that complex cement systems that are undergoing hydration generate coupled dissolution crystallization reactions. While the actual solid (*i.e.*, cement) phases are distinctly different from geochemical systems involving minerals, the principal behavior is very similar. Therefore, it is possible to apply the same experimental, analytical and theoretical strategies that have been applied successfully to diverse geochemical problems. Second, at the same time, it is important to avoid the same traps and faults that have hampered our approach to geochemical processes. We have discussed a number of potential problems, mainly the temptation to apply TST to overall reaction kinetics or to assume or postulate "obvious" reaction mechanisms and surface complexes. Unsolved problems include the correct measurement of surface area and its change during the reaction, as well as our inability to quantify $f(\Delta G)$ for the reactions of interest.

These above are certainly challenges to be tackled and solved in the future. Some problems that we highlighted may even seem discouraging, particularly if we cannot use strategies that have been established in the literature but have proven to lead to a dead end. As an alternative, we suggest a new

integrated approach that seeks to combine molecular modeling techniques, particularly kMC with vertical scanning interferometry, atomic force microscopy, XPS, XRD and other techniques. This approach sacrifices closed form equations, often called rate laws that fit the laboratory-generated data but often fail to predict or explain reaction kinetics correctly. Instead, we suggest an approach that utilizes open form equations and builds on a stochastic many-body treatment of complex systems. Although it may prove difficult or impossible to predict overall rates immediately, these strategies should provide critical insights into the basic reaction mechanisms and the effect of inhibitors and accelerators and the interaction between various cement phases, *i.e.*, C_3A and gypsum. In this way we will be able to gain the critical insight that will allow us to build a fundamental understanding of cement hydration reactions and their dynamic behavior.
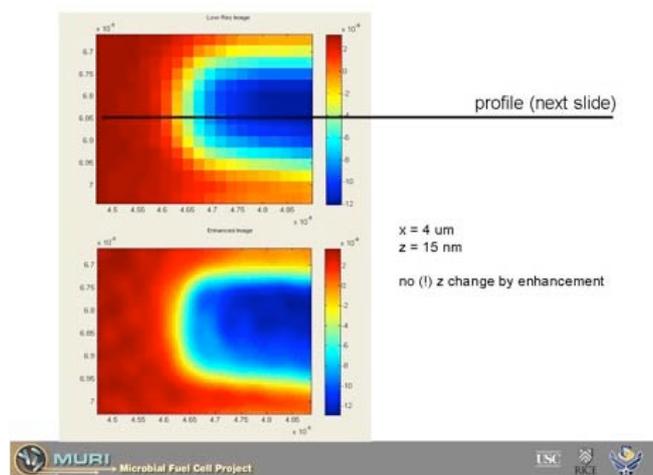

Fig. 11. *Two measurements (optical measurement and 4x enhancement) of another certified step height standard. Note that the flanks are much better resolved in the deconvolved image.*
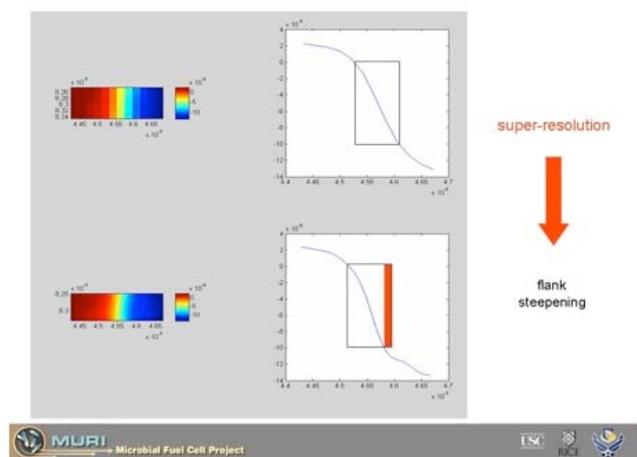

Fig. 12. *Plot demonstrating the improvement of flank steepness. The chart shows the profile line shown in Fig. 11. Improvement of flank steepness is a quantitative measure for resolution improvement.*

International Summit on Cement Hydration Kinetics and Modeling, July 27-29, 2009.

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