DE- SC0004118 (Wong & Lindquist).

Final Report: In the context of CO_2 sequestration, the overall objective of this project is to conduct a systematic investigation of how the flow of the acidic, CO_2 saturated, single phase component of the injected/sequestered fluid changes the microstructure, permeability and strength of sedimentary rocks, specifically limestone and sandstone samples. Hydromechanical experiments, microstructural observations and theoretical modeling on multiple scales were conducted. We summarize below the key accomplishments of our project:

(1) A major challenge in characterizing the pore geometry of carbonate rock is its complexity: the depositional environment and diagenesis exert significant genetic influence over the development of texture and fabric of a carbonate rock, which can in turn modify both the size and connectivity of the pore space in a relatively rapid and drastic manner. The pore geometry of a porous carbonate rock is very complex and its 3D imaging poses significant challenge. Nevertheless, microCT imaging has proved to be useful for characterizing the preexisting pore structure and mechanical damage. We studied the pore structure in intact and inelastically compacted Indiana limestone. Guided by detailed microstructural observations, we developed an effective technique to segment the CT image into three domains: solid grains, macropores and an intermediate zone dominated by microporosity. The macropores were individually identified by morphological processing and their geometric attributes quantitatively characterized. Our data revealed a significant reduction of the number of macropores in hydrostatically and triaxially compressed samples with respect to the intact material, in agreement with previous microstructural analysis and a micromechanical model for cataclastic pore collapse. The intermediate (microporosity) domains remained interconnected in compacted samples. Our data suggest that the inelastic compaction in Indiana limestone is manifested by not only a decrease in the volume fraction of the microporosity backbone, but also a corresponding decrease in its thickness. Our research was presented in a manuscript by *Ji et al.* [2012]. In parallel, a study was recently conducted by *Ji et al*. [2014] on the significantly more porous Majella limestone, which has revealed subtle differences in pore structure.

(2) We have developed reactive network flow models to study upscaling of reaction rates from pore-to-core scale. The current application has concentrated on reactions pertinent to CO_2 sequestration in sandstone deposits. There is a high likelihood that carbonate cap rock will be encountered in realistic scenarios of CO_2 sequestration – the need for an accurate understanding of in-situ reaction rates can be addressed through the type of network flow models we can build. Initial work [*Kim and Lindquist*, 2011; *Kim et al*., 2011] has studied the effects of mineral heterogeneity (through realistic mineral maps captured through microCT), uncertainty in chemical kinetic models, and flow rate on core-scale bulk reaction rates. Our initial models have the deficiency of not capturing geometrical changes that accompany dissolution and precipitation (porosity increase/decrease, permeability increase/decrease, new channel connections/loss of channel connection). This was tackled with a dissolution model that accurately follows the geometry of the actively dissolving minerals, and a model for highly caustic solution flow through unconsolidated soils typical of the Hanford site. Initial work documenting

physical changes under dissolution and precipitation in this flow is described in *Crandell et al*. [2012].
(3) MicroCT can be used to characterize the geometry of the pore space of a sedimentary rock, with resolution in porous sandstone that may be sufficiently refined for the realistic simulation of permeability based on the 3D image. Significant advances have been made on the characterization of pore size distribution and connectivity, development of techniques such as lattice Boltzmann method to simulate permeability, and its upscaling. *Sun, Andrade and Rudnicki* (2011) recently proposed a multiscale method that dynamically links these three aspects, which were often treated separately in previous computational schemes. After geometric attributes of the connected pore space had been extracted, a hybrid lattice Boltzmann/finite element scheme was developed to calculate a homogenized effective permeability. In collaboration with Waiching Sun of Sandia National Lab, we applied this hybrid technique to the microCT data of Fontainebleau sandstone acquired by *Lindquist et al*. (2000), which has proved to be computationally efficient and our simulations has elucidated the relation among permeability, pore geometry and connectivity. We have extended the computational scheme to also include the hybrid modeling of electrical conductivity and formation factor, which would allow one to consistently simulate the hydraulic and electrical transport using the multiscale method. The results were presented in the 2012 BES workshop in Gaithersburg, and are written up in a manuscript for submission to *J. Geophys. Res.*
(4) Digital image correlation is a technique that is widely used in experimental mechanics to map out the spatial distribution of strain, and it has recently been successfully applied to porous limestone. There is a paucity of data regarding the failure mode of porous limestone, especially in the transitional regime between brittle faulting and cataclastic flow. A study using DIC was conducted on the Majella limestone [*Ji et al*., 2014]. Our first application of 3D-volumetric DIC to a very porous limestone has demonstrated the feasibility of mapping out the subtle development of strain localization, and it promises to be an effective imaging tool for strain localization in other carbonate rocks over a broad range of porosity. Our study demonstrates that strain localization may develop very early at relatively small strains of ~1%, in both the brittle faulting and transitional regimes. The DIC analysis indicates that the localized strains are primarily in the forms of shear and compaction. These observations place useful insights into the theoretical analysis of strain localization.
(5) To characterize the chemical effects on mechanical strength, we have undertaken a series of mechanical tests on limestone samples saturated with deionized water and inert gas. In Wong's lab, previous investigation of carbonate rock deformation has focused on nominally dry sample, and published data on water-saturated samples are not always in agreement. In our investigation, we have systematically isolated and characterized the chemical and mechanical effects. Two related papers [*Vajdova et al*., 2012; *Wong and Baud*, 2012]. Our data indicate chemical effects which are fundamentally different in the brittle faulting and cataclastic flow regimes, which may be attributed to difference in fracture mechanics in the microporosity and macroporosity. We are in the process of writing up the results in a manuscript to be submitted.

Crandell, L., C.A. Peters, W. Um, K.W. Jones and W.B. Lindquist, Changes in the pore network structure of Hanford sediment after reaction with caustic tank wastes, *J. Contam. Hydrol.*, **131** (2012) 89.

Ji, Y., P. Baud, V. Vajdova, and T.-f. Wong, Characterization of pore geometry of Indiana Limestone in relation to mechanical compaction, *Oil & Gas Sci. and Tech. - Rev. IFPEN*, **67**, 753-775, 2012.

Ji, Y., S.A.Hall, P. Baud, and T.-f. Wong, Characterization of pore structure and strain localization in Majella limestone by X-ray computed tomography and digital image correlation, *Geophys. J. Int.*, in press, 2014.

Kim, D. and W.B. Lindquist, Dependence of pore-to-core up-scaled reaction rate on flow rate in porous media, *Trans. Porous Media*, **89** (2011) 459.

Kim, D., C.A. Peters and W.B. Lindquist, Upscaling geochemical reaction rates accompanying acidic CO_2-saturated brine flow in sandstone aquifers, *Water Resour. Res.*, **47** (2011) W01505, doi:10.1029/2010WR009472.

Vajdova, V., P. Baud, L.Wu, and T.-f. Wong, Micromechanics of inelastic compaction in two allochemical limestones, *J. Struct. Geol*., **43**, 100-117, 2012.

Wong, T.-f. and P. Baud, The brittle-ductile transition in porous rock: A review, *J. Struct. Geol*., **44**, 25-53, 2012.