

UNIVERSITY OF SOUTH FLORIDA

Creation of Carbon Sequestration Data, Technologies and Professional Cohorts for Florida

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Description: Rising concerns over increasing levels of green house gases, especially carbon dioxide, have led to suggestions to capture carbon dioxide at fixed sources, such as fossil fuel power plants, and sequester the carbon for millennia by injecting it underground. Florida overlies many thousands of feet of carbonate rocks which may be suitable for geologic sequestration of carbon dioxide. This project will investigate the potential for geologic sequestration of carbon dioxide in Florida, the physical and chemical changes that may occur as a result of injection, assess the potential for escape of injected carbon dioxide, determine the risk, if any, to aquifer systems used for water supplies, develop methodologies for Florida utilities to predict the performance and risks of proposed sequestration projects, and educate a cohort of geologic sequestration professionals to create a carbon sequestration industry in Florida.

Budget: \$147.360

Universities: USF

External Collaborators: Tampa Electric Company (TECO)

Progress Summary

In the past year, we have made significant progress with our analysis of the physics and chemistry of supercritical CO₂ injection into deep saline aquifers, with particular application to the formations identified in Florida. We have begun development of a computational model that provides a pore-scale description of the displacement of native brine by injected CO₂. The model is based on the lattice Boltzmann method for simulating fluid flows in complex geometries. Also, we have developed a geochemical model that predicts the extent of mineral dissolution or precipitation when injected CO₂ dissolves into the brine. Results of model simulations suggest that, when supercritical CO₂ dissolves in native brine, the resulting drop in solution pH induces the minerals dolomite and calcite to dissolve. The release of calcium ions into the brine then induces precipitation of the mineral gypsum. However, the volumes of minerals dissolved and precipitated are small, representing a very small fraction of the aquifer volume, and thus it does not appear that either mineral dissolution or mineral precipitation should prevent the success of CO₂ sequestration in Florida.

A major evaluation of geologic units suitable for geologic sequestration has been completed. It contains three individual reports, one on the Sunniland Limestone of the South Florida Basin, one on the Upper Cretaceous-Paleocene Cedar keys-Lawson injection zone, and a review of other potential sequestration reservoirs in peninsular Florida. All three reports will be published in 2011 by the Florida Geological Survey under the auspices of a grant from the US Geological Survey.

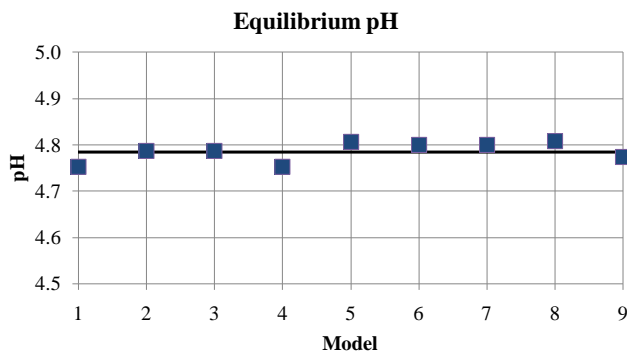
Geochemical modeling of the interactions of waste streams and supercritical CO₂ with brines in saline aquifers and the carbonate minerals of the matrix continues. This modeling is supported in part by TECO Energy and ECT, a consulting firm working with TECO. As of October, 2010, a deep injection well is being drilled at the Polk Power Station (PPS) in Polk County. The USF/FESC sequestration team is in close communication with TECO and ECT as the well progresses. Initially, the well is to be used to co-inject municipal wastewater and a PPS waste stream into the Cedar Keys-Lawson injection zone identified at the PPS by the USF CCS team.

RTI of Raleigh North Carolina has announced funding from DOE to conduct a pilot study of carbon capture and sequestration at PPS, and a prototype carbon dioxide capture system is being installed at the Big Bend coal-fired power plant in Apollo Beach, Florida. Information developed by USF in recent studies has allowed these advanced CCS projects to be planned and funded in Florida.

2010 Annual Report

Physical and Chemical Modeling of Injection of Supercritical CO₂

To assess the feasibility of storing CO₂ in the Cedar Keys / Lawson saline aquifer system, we must estimate the geochemical reactions that are likely to result from CO₂ dissolution into the native brine. We built a geochemical model capable of predicting the reactions between three minerals (calcite, dolomite, and gypsum) and 28 aqueous species. We assessed different thermodynamic sub-models which

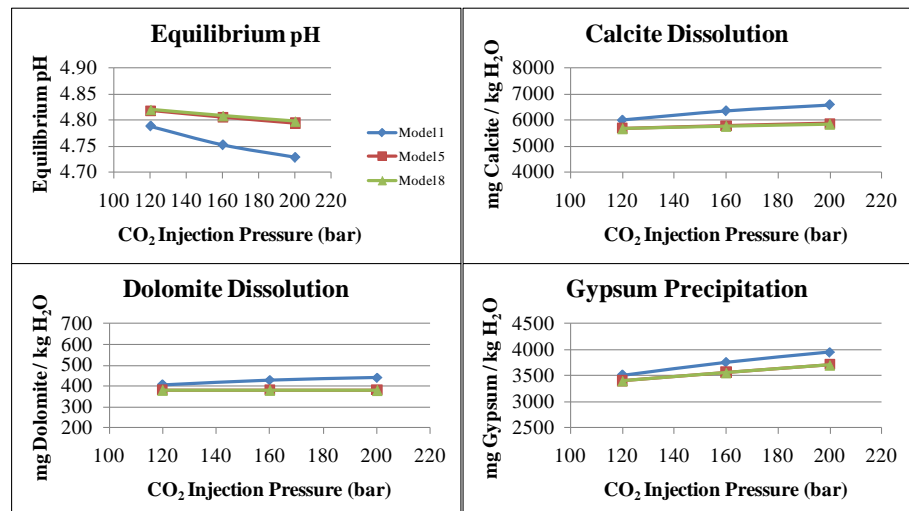


have been proposed for estimating properties such as activity coefficients, fugacity of supercritical CO₂, and aqueous solubility of CO₂. Nine different combinations of thermodynamic sub-models were tested. We found that the different thermodynamic sub-models all yield similar predictions of the effects of CO₂ injection, i.e., the choice of a particular method for estimating the thermodynamic parameters does not have a strong effect on the model results; see the accompanying Figure. The similar results

obtained from the different thermodynamic sub-models may indicate that all the models are acceptable. The geochemical model predicts that calcite and dolomite dissolve upon injection of supercritical CO₂, and gypsum precipitates.

The geochemical model predicts that the extent of mineral dissolution and precipitation is

relatively sensitive to the temperature in the aquifer and to the salinity (ionic strength) of the brine, but is relatively insensitive to the initial pH of the brine and, surprisingly, to the injection pressure of the CO₂ (see Figure). In all cases tested, the model predicts that formation porosity will increase due to the dissolution of calcite and dolomite. However, in all simulations, the predicted change in formation porosity due to mineral dissolution is very small, indicating that CO₂ injection is not expected to significantly alter the porosity of the repository formation.



$\epsilon_{INITIAL}$	S_{RES}	Init. pH	CO ₂ Injection Pressure (bar)	Salinity	Temp. (°C)	Estimated $\Delta\epsilon$		
						Model 1	Model 5	Model 8
0.2	0.3	6.5	160	10%	45	5.0E-05	4.1E-05	4.1E-05
0.2	0.3	7.5	160	10%	45	5.0E-05	4.2E-05	4.1E-05
0.2	0.3	8.5	160	10%	45	5.0E-05	4.2E-05	4.1E-05
0.2	0.3	7.5	120	10%	45	4.8E-05	4.4E-05	4.3E-05
0.2	0.3	7.5	200	10%	45	5.0E-05	4.0E-05	3.9E-05
0.2	0.3	7.5	160	5%	45	5.3E-05	4.4E-05	4.4E-05
0.2	0.3	7.5	160	15%	45	4.8E-05	4.1E-05	4.1E-05
0.2	0.3	7.5	160	10%	35	7.0E-05	5.7E-05	5.6E-05
0.2	0.3	7.5	160	10%	55	3.6E-05	3.1E-05	3.1E-05

Geochemical Modeling of Supercritical CO₂ Interactions with Brine and Carbonate Minerals

Geologic sequestration of carbon dioxide (CO₂) in a deep, saline aquifer is being proposed for a power-generating facility in Florida as a method to mitigate contribution to global climate change due to greenhouse gas (GHG) emissions. The proposed repository is a briny, dolomitic-limestone aquifer with anhydrite inclusions contained within the Cedar Keys/Lawson formation of Central Florida.

Estimating the storage capacity per unit aquifer volume requires accurate assessments of the mass of CO₂ stored via each of the three storage avenues: bulk CO₂ in pore space, CO₂ dissolved in brine, and precipitation of carbonate minerals. To begin to quantify the storage due to CO₂ dissolution, off-the-shelf geochemistry software (OTSGS) was used to simulate brine and CO₂ interactions, and the results were compared to the aqueous CO₂ concentrations calculated by the Duan et al. (2006) parameterization of experimental data, which closely fits published solubility of CO₂ in brine containing sodium, chloride, calcium, magnesium, and sulfate ions over a wide range of concentrations, temperatures, and CO₂ pressures. Figure 1 shows the findings that CO_{2(aq)} predictions from various OTSGS packages range from negative 40% to positive 40% relative error (taking the Duan et al. results as the correct values), demonstrating that OTSGS must be scrutinized carefully for applicability to high CO₂ pressure, high salinity conditions.

Thermodynamic modeling was used to investigate the geochemical equilibrium reactions for the minerals calcite, dolomite, and gypsum with 28 aqueous species for the purpose of determining the sensitivity of mineral precipitation and dissolution to the temperature and pressure of the aquifer and the salinity and initial pH of the brine. In-house computer codes were developed to utilize different theories for estimating CO₂ fugacity, solubility in brine, and chemical activity. Nine different combinations of thermodynamic models (see Table 1) were tested and predicted results are in good agreement, so the particular choice among the different theories is relatively insignificant. It is **predicted that calcite and dolomite will dissolve and gypsum will precipitate**, and over the range of values examined, it is found that net mineral dissolution and precipitation **is relatively sensitive to temperature and salinity, insensitive to pressure and initial pH, and does not indicate that significant changes to porosity will occur.**

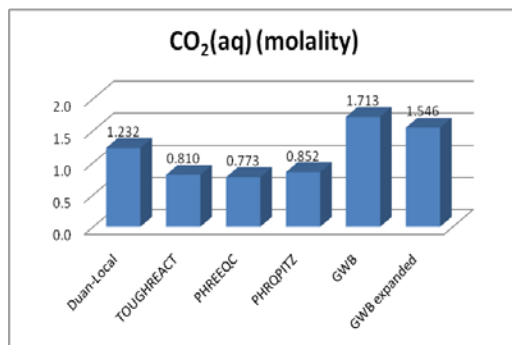


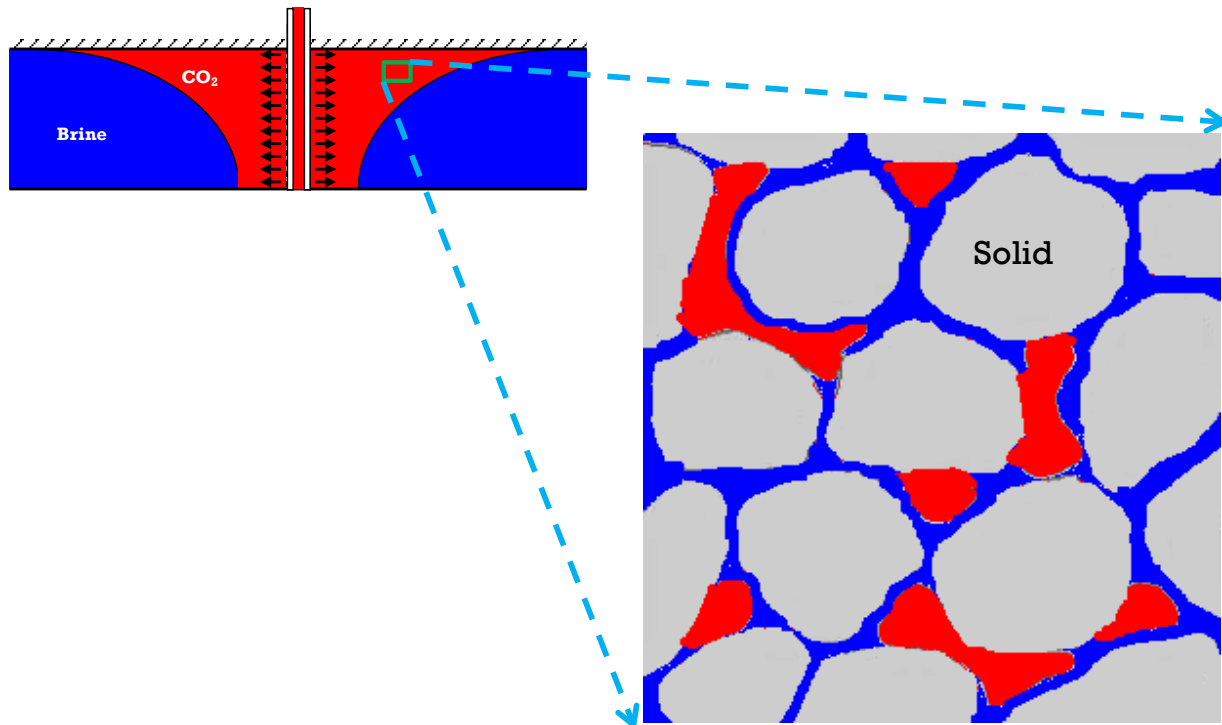
Figure 1: Comparison of different OTSGS predictions of CO₂ dissolution in 15% salinity brine, 45°C, and equilibrated with 180 bar supercritical CO₂ to the “Duan-Local” codes benchmark.

Model	Sub-models for CO ₂ thermodynamic parameter estimation		
	CO _{2(aq)} Activity Coefficient	CO _{2(g,sc)} Fugacity Coefficient	CO _{2(aq)} Solubility
1	Drummond (1981)	Spycher & Reed (1988)	Equilibrium Coefficient
2	Drummond (1981)	Duan and Sun (2006)	Equilibrium Coefficient
3	Rumpf et al. (1994)	Duan and Sun (2006)	Equilibrium Coefficient
4	Rumpf et al. (1994)	Spycher & Reed (1988)	Equilibrium Coefficient
5	Duan and Sun (2003)	Duan and Sun (2006)	Duan and Sun (2003)
6	Drummond (1981)	Duan and Sun (2006)	Duan and Sun (2003)
7	Drummond (1981)	Duan and Sun (2006)	Spycher and Pruess (2005) adaptation of Duan and Sun (2003)
8	Rumpf et al. (1994)	Duan and Sun (2006)	Spycher and Pruess (2005)
9	Rumpf et al. (1994)	Spycher & Reed (1988)	Spycher and Pruess (2005)

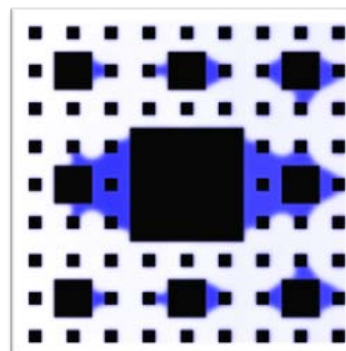
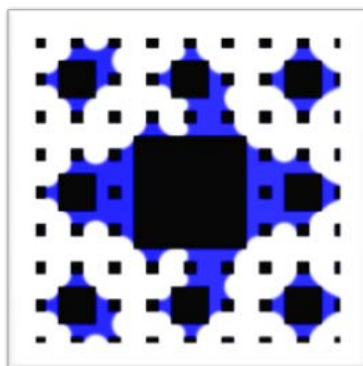
Table 1: Combinations of Sub-Models for CO₂ Thermodynamic Parameter Estimation

Physical Modeling of Injection of Supercritical CO₂

The entrapment of brine in pores after injection of CO₂ is controlled by capillary forces and by the inertial force driving CO₂. The entrapped/residual brine will be a site for the geochemical reactions described elsewhere in this report. Pore-scale understanding of the displacement of brine by CO₂ is critical to evaluate the storage efficiency of the aquifer and to determine the extent to which mineral dissolution/precipitation will affect the formation's permeability. We have begun development of a multiphase flow model, based on the lattice Boltzmann method (LBM), that can describe pore-scale displacement of brine by invading CO₂.



LBM is a numerical method based on kinetic theory of gas. It is a mesoscopic approach, i.e., it is applicable at a scale between molecular dynamics and familiar continuum approaches, which makes it



extremely powerful for the simulation of fluid flows. Furthermore, LBM is easily amenable to complicated geometries such as porous media. The LBM model has so far been applied to simulate the displacement of brine

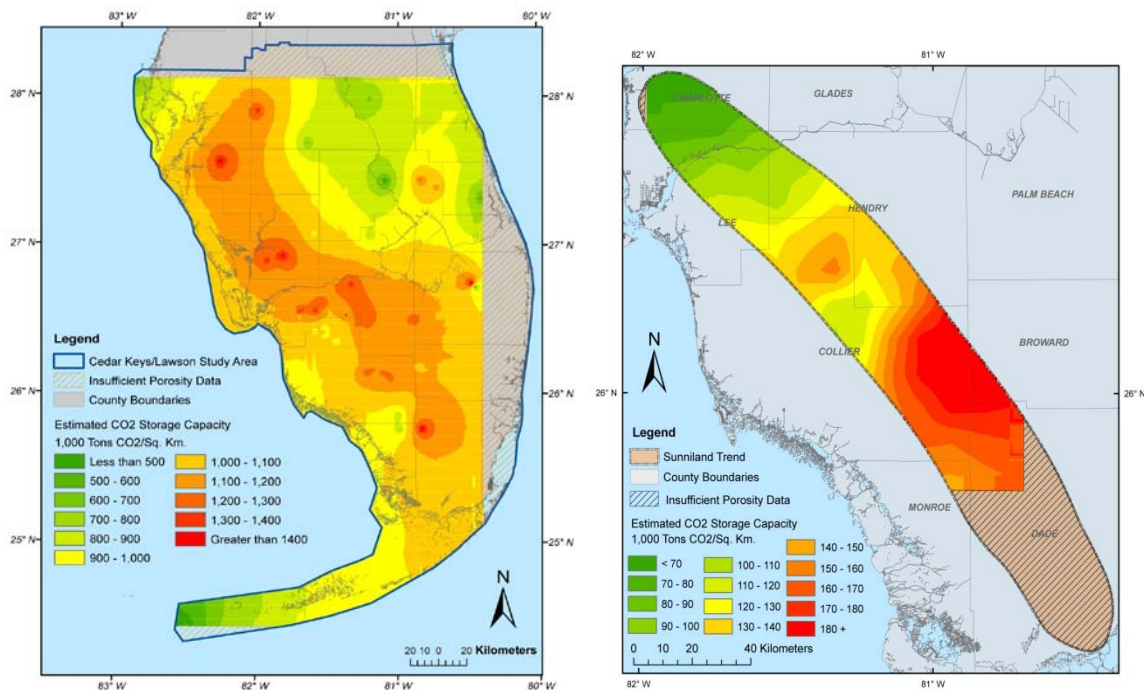
by CO₂ in fractal porous media (see Figure). This simplified geometry allows us to explore factors such as the ratio of brine viscosity to CO₂ viscosity; the two figures are conducted at different viscosity ratios.

Future work will focus on coupling the LBM multi-phase flow model with the geochemical models.

Geologic Carbon Sequestration in Florida

From November, 2009 to October, 2010, three reports were completed on potential geologic reservoirs for the long-term geologic sequestration of carbon dioxide. These three reports were prepared by Tina Roberts-Ashby, USF Geology PhD student supported by the FESC, and Dr. Mark Stewart, USF Geology professor. The two principal geologic reservoirs investigated in the first two reports are the Sunniland Formation of southwest Florida, and the Cedar Keys-Lawson injection zone (CKLIJ) of central and south Florida. The Sunniland has the smaller storage potential, about 70-180 tons CO₂/km², with the highest storage capacities in Collier County. The Sunniland Formation has the potential for concurrent production of 20-30 million barrels of oil through enhanced oil recovery during CO₂ injection. The CKLIJ has very high storage capacities, >1000 tons CO₂/km². The total storage capacity of the CKLIJ in central and south Florida exceeds 500 million tons of CO₂. The CKLIJ could accept the annual CO₂ production of more than 100 1000MW coal-fired power plants for 50 years.

The third report is a reconnaissance survey of other potential geologic sequestration reservoirs in Florida. Other promising reservoirs are several Cretaceous age dolomitic zones above and below the Sunniland injection zone, and the very extensive Cretaceous-Paleocene Rebecca Shoal Reef, an ancient atoll that underlies both the east and west coasts of the Florida Peninsula. All three reports will be published online by the Florida Geological Survey in early 2011.



Capture of Carbon Dioxide from Power Plant Flue Gas

A goal of this research is to develop a sorbent that will effectively and inexpensively capture carbon dioxide from power plant flue gas. Current efforts include investigating the metal oxide to develop a sorbent with a better conversion stability and higher conversion rate. This was done by applying calcium-carbonate mixture to alumina fabric. To examine how well the material is able to absorb CO₂, 0.5g of calcium carbonate was

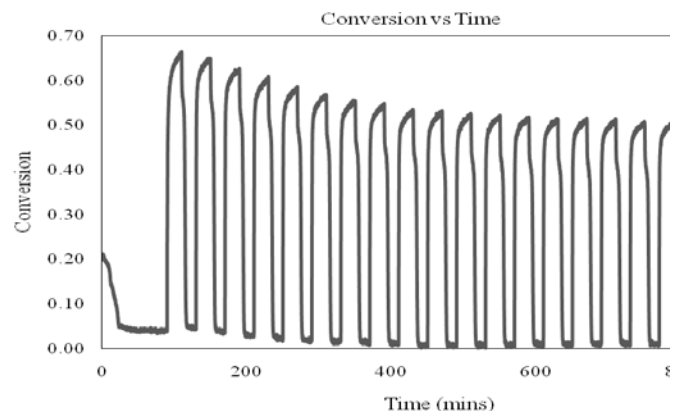


Fig. 1 Conversion of Calcium carbonate over 21 cycles

added to alumina fabric and placed in the furnace for 20 hours. The prepared sample was evaluated under isothermal condition at 750 C while the pressure of CO₂ was 80 psi. Fig. 1 shows the conversion of calcium carbonate over 21 cycles. As can be clearly seen, the maximum conversion decreases over the first few cycles and then stabilized around 53%.

It is expected that changing the operating conditions would affect the behavior of the material. Therefore, conversion of this material was examined at three different temperatures. As shown in Fig. 2, decreasing the temperature from 750⁰ C to 700⁰ C led to a dramatic increase in the maximum conversion from 0.53 to 0.72 while the time required for calcination increased from 5.5 to 11.7 min. Further decrease in the temperature did not affect the maximum conversion much while it had an undesirable effect on the calcination time. Moreover, the effect of CO₂ pressure is shown in Fig.3. According to the figure, changing the pressure from 80 psi to 110 psi led to a dramatic increase in the maximum conversion from 0.53 to 0.71.

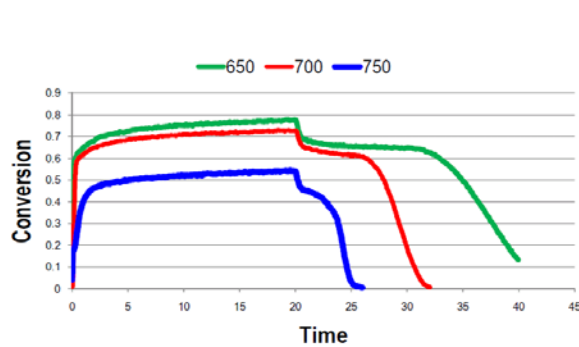


Fig. 2 Variations of conversion in different temperatures

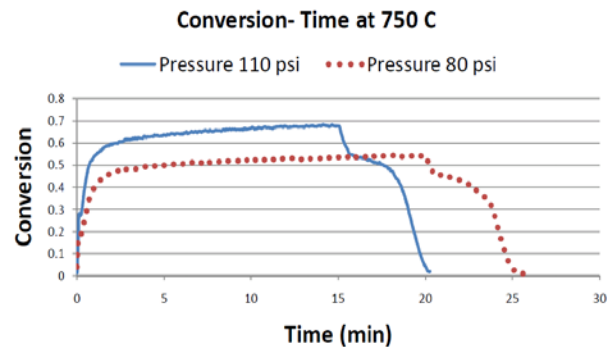


Fig. 3 Variations of conversion in two different pressures

The gas–solid CO₂–CaO reaction proceeds through two rate controlling regimes, namely reaction control regime and diffusion control regime. Based on these facts, a shrinking model is obtained. Fig.4 shows how well the model fits the experimental data.

Reaction control

$$X = 1 - \left(1 - \frac{kt}{3}\right)^3 \quad k=0.043988$$

Diffusion Control

$$-3(1 - X)^{\frac{2}{3}} + 2(1 - X) = 2kt - 1 \quad k=0.000514$$

$$k = \frac{12D_e C_{Ag}}{\rho R^2}$$

