CATO-2 Deliverable WP 3.4-D02
Progress report: Application of advanced materials/treatments for abandonment and mitigation

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1 Executive Summary (restricted)

Work on materials and treatments for improving well integrity, and for mitigating any leaks that might occur, is funded at Utrecht University (UU), IF Technology / Well Engineering Partners (IF-WEP), and TU Delft (TUD).

During Year 1 of CATO-2, preparatory work has been conducted at UU with the aim of identifying mineral additives to wellbore cements (or injection fluids) that can act as clogging agents upon reaction with CO_2. Further preparatory work at UU has included assessing the geochemical and geomechanical effects of such reactions, and setting up equipment to study them. A variety of powdered minerals, such as olivine, serpentine and calcium hydroxide have been identified from the literature as potentially promising additives, alongside fly ash. Preliminary experiments performed on olivine and fly ash have also shown that reaction is rapid enough to be potentially useful and that significant reduction in permeability results. However, theoretical studies have indicated that the swelling that accompanies reaction can have both beneficial (clogging) and detrimental (fracturing) effects. Optimising clogging effects over fracturing will therefore be key to the work planned for Years 2-5.

IF-WEP will review current industry best practices for plugging wells for standard and more advanced materials, applied in a CO_2 environment. This serves as a basis for identifying any shortcomings and possible new materials. Work will commence in year 2.

Work at TU Delft will begin in year 2, and will focus on assessing best practices and promising research ideas for remediation of casing leaks in the petroleum industry, and experimental study of flow of non-Newtonian (remediation) fluids through cracks and porous media.

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2010.08.24		Final deliverable	

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2 Applicable/Reference documents and Abbreviations

2.1 Applicable Documents

	Title	Doc nr	Version date
AD-01	Beschikking (Subsidieverlening CATO-2 programma verplichtingnummer 1-6843	ET/ED/9078040	2009.07.09
AD-02	Consortium Agreement	CATO-2-CA	2009.09.07
AD-03	Program Plan	CATO2-WP0.A-D.03	2009.09.29

2.2 Reference Documents

	Title	Doc nr	Version/issue	Date

2.3 Abbreviations

IF-WEP	IF Technology / Well Engineering Partners
UU	Utrecht University
TUD	Delft University of Technology

3 General Text

Work on this task will proceed at three locations, i.e. at Utrecht University (UU), IF Technology / Well Engineering Partners (IF-WEP), and TU Delft (TUD). Funds for this task begin largely within Year 2, so this progress report for Year 1 comprises a brief account of preparatory activities executed to date, plus brief summaries of plans for the coming four years of the CATO-2 project.

3.1 Utrecht University: Mineral additive studies

1) The UU contribution to work on advanced materials and treatments for well abandonment and leak mitigation under WP 3.4 has two main aims:Lab assessment of the effects of mineral additives for promoting sealing or clogging, and
2) Extending modelling tools to include the effects of mineral additives on reaction and transport within wellbore systems, and to assess the impact on performance.

These aims are distributed over the full duration of CATO-2, and will be executed largely in the framework of the PhD and PD positions recently approved to start at UU between September 2010 and January 2011.

During Year 1 of CATO-2, preparatory work has been conducted at UU on the following aspects of Aim 1 above:

a) Identification of mineral additives to cement (or injection fluids) that can act as clogging agents through carbonate precipitation, as well as buffering wellbore zone pH
b) Identification of waste materials that might fulfill this function
c) Consideration of the likely geomechanical effects of clogging reactions leading to solid volume increase
d) Setting up an experimental design to assess reaction rates and geomechanical effects

From studies of the literature on surface and subsurface mineralisation of CO_2 by reaction with natural minerals (Lackner et al. 1995, Huijgen et al. 2006, Gerdemann et al., 2007), the following minerals have been identified as possible additives to cement, or as possible suspensions suitable for injection as leak-stoppers:

- Powdered olivine
- Powdered serpentine
- Powdered wollastonite
- Powdered hydroxides of calcium, magnesium and iron

Possible industrial waste products that could potentially be of use include:

- Fly ash (calcium and iron hydroxide and chloride rich)
- Crushed steel slag (calcium silicate rich).

All of the above reactions are capable of precipitating stable carbonates in a downhole environment in the presence of water and supercritical CO_2. In most cases, reaction leads to a significant increase in solid phase volume, which can potentially clog pores, cracks or de-bonded wellbore interfaces. Some examples of interesting reactions are given below (see Hangx & Spiers 2009):

Olivine: $Mg_2SiO_{4\,(s)} + 2CO_{2\,(g)} + 2H_2O_{(l)} \leftrightarrow 2MgCO_{3\,(s)} + H_4SiO_{4\,(aq)}$

Wollastonite: $CaSiO_{3\,(s)} + CO_{2\,(g)} + 2H_2O_{(l)} \leftrightarrow CaCO_{3\,(s)} + H_4SiO_{4\,(aq)}$

Serpentinite: $Mg_3Si_2O_5(OH)_{4\,(s)} + 3CO_{2\,(g)} + 2H_2O_{(l)} \leftrightarrow 3MgCO_{3\,(s)} + 2H_4SiO_{4\,(aq)}$

In the case of the olivine reaction, the increase in solid volume is around 80%.

However, if precipitating mineral interfaces remain wetted as reaction proceeds, and if high supersaturations of the precipitating phases build up in the aqueous phase, then theoretical studies indicate that significant stresses may build up as the reaction products "swell". Indeed, following Spiers and co-workers (De Meer & Spiers 1997, Spiers et al. 2004), normal stresses can be generated with a magnitude given by

$$\sigma_n \approx \Delta C / (C_0 R T \Omega)$$

where ΔC is the supersaturation of the precipitating phae, C_0 is its solubility, Ω is its molar volume, R is the gas constant and T is absolute temperature. Such "force of crystallization" effects might have the potential to fracture the caprock seal around the wellbore by the process of reaction-driven fracture. Further attention is therefore needed for the competition between the possible beneficial and detrimental effects of additive reactions – from both geomechanical and transport properties perspectives. This will form a significant component of UU work in the coming years.

To date, a variety of experimental methods have been set up at UU to conduct reaction experiments on selected additives, and to measure volumetric changes and stresses developing during unconfined and confined reaction respectively. These include straight-forward autoclave and cold-seal pressure vessels for hydrostatic reaction experiments, as well as 1-D piston-cylinder equipment for measurement of reaction-induced stresses under confined conditions. Preliminary experiments on olivine and fly ash have shown that reaction is rapid enough to be potentially useful and that significant reduction in permeability results from confined reaction.

In Years 2-5, this work will continue, focusing on Aims (1) and (2) given above, as described in the PhD and PD projects allocated to UU for CATO-2b.

3.2 IF Technology / Well Engineering Partners: Best Practices for Plugging Leaks

IF-WEP will mainly focus on current oil & gas industry best practices for standard and non-standard plugging materials, applied in a CO_2 environment.

IF-WEP has experience with plenty of plugging materials in actual field jobs, for primary cement jobs as well as for well abandonments. Also IF-WEP have a good insight in current industry best practices for standard plugging materials. The effort will focus on cement, CO_2 resistant cement, cementing practices and high-end materials (for instance resins). This work will complement that of UU and in particular of TUD.

3.3 TU Delft: Current Best Practices and Innovative Methods of Plugging Leaks

Work will proceed along two lines. First, we will survey contacts in the international petroleum industry for information on best current practices for materials and methods for casing-leak remediation and promising avenues of research. Casing leaks are a major issue in the petroleum industry, both because of environmental concerns (witness the recent Deepwater Horizon tragedy in the Gulf of Mexico) and because of loss of production and unintended intermingling of fluids from different producing intervals. A quick search of OnePetro, the technical-paper database for the petroleum industry, finds 16 papers with the phrase *casing leak* in the title in the last 10 years, while a Google search of "well casing leak" produces 114,000 hits. The petroleum industry has injected CO_2, H_2S and other acidic gases into petroleum reservoirs for enhanced oil recovery for decades, and has had to cope with possible leaks of these gases around wells. The time frame for permanent CO_2 sequestration poses challenges beyond those of an EOR process, but much of the technology for remediation would be the same.

Second, we have recruited a PhD student with expertise in flow of nanoparticles, colloids and complex materials to conduct research on flow in cracks and porous media. CATO-2 provides a part of the funding of this research. This student will investigate experimentally the flow of non-Newtonian fluids through cracks and other porous media, with a particular focus on flow of colloidal dispersions stabilized by nanoparticles.

3.4 References

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