

Enhanced in-situ leaching mining– Modeling with TOUGHREACT

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Einige Rohstoffe wie z.B. Seltene Erden Elemente (SEE) kommen nur in relativ geringen Konzentrationen vor und machen Bergbau und Aufbereitung schwierig und teuer. Vor kurzem hat die Europäische Gemeinschaft festgestellt, dass für 14 ökonomisch wichtige Rohstoffe einschließlich SEE ein hohes Risiko hinsichtlich der Versorgungssicherheit besteht. Daher wird hier ein innovativer Ansatz vorgestellt, der zu einer anwendbaren Prozesstechnologie entwickelt werden kann. Er basiert auf der Verwendung von überkritischem Kohlenstoffdioxid ($scCO_2$) zur Stimulation von geringdurchlässigen Gesteinen und verbindet dies mit der Minimierung des Umwelteinflusses, der mit klassischem Bergbau und Erzaufbereitung verbunden ist. Ziel dieser Studie ist es, den physiko-chemischen Einfluss von $scCO_2$ auf Carbonate als Ressource für z.B. SEE mittels numerischer Simulation mit TOUGHREACT zu untersuchen. Kohlensäure bildet sich, wenn $scCO_2$ mit Wasser in Berührung kommt. Infolge des Kontaktes zwischen Kohlensäure und Carbonat kommt es zur Carbonatauflösung. Selbst eine kleine Veränderung der Porosität bewirkt eine Vergrößerung der Durchlässigkeit. Durch die Injektion von $scCO_2$ kommt es zu einem Druckanstieg, der zu einer Öffnung von bestehenden Rissen bzw. zur Bildung neuer Risse führen kann, wodurch letztlich die Porosität und Permeabilität zunehmen.

Some raw materials like rare earth elements (REE) occur in rather low concentrations which makes mining and extraction difficult and costly. Recently the European community has identified 14 economically important raw materials including REE which are subjected to a high risk of supply interruption. Herewith, an innovative approach is proposed that can be developed into an applicable process technology. It makes use of the capability of supercritical carbon dioxide ($scCO_2$) to stimulate low-permeability rock while having the ability to considerably reduce negative effects on the environment due to ore mining and processing compared to conventional methods. The objective of this paper is to study the physical and chemical impact of $scCO_2$ on carbonate rock as a minable ore reservoir for e.g. REE through numerical simulations by means of TOUGHREACT. Carbonic acid is formed when $scCO_2$ gets mixed with water; as a result calcite dissolution occurs. Additionally, dissolution of calcite creates voids and increases porosity. Even a small increase in porosity has significant effect on enhancement of permeability. With the injection of $scCO_2$ there is an increase of pressure inside the layer which may lead to opening up the existing fissures and also creating new ones which in turn will further enhance porosity and permeability.

1. Introduction

Economically attractive processing of ores from mineral deposits on a commercial scale requires a technical enrichment of mineral resource components within the ore to certain concentrations which individually depend on the element to be recovered and the market price. Raw materials like rare earth elements (REE) may occur in rather low concentrations. Hitherto REE are imported from China at a large scale which dominates the world market in this field by selling raw materials, intermediates or final goods like electronic devices. It is foreseeable that the need of European countries for REE will keep increasing in future and consequently the raw material supply will become a strategic interest of European economy, as i.e. reflected in the European Raw Material Initiative of the European Union or in the German *Rohstoffinitiative*.

It is for these reasons in the utmost European interest to develop innovative technologies for the mining and processing of REE and other materials recovered through mining activities from European sources. In fact Europe has a significant number of low grade REM deposits, but it lacks the

technology to commercially process low grade ores. The European raw material recovery interests are accompanied by the necessity to reduce the interference of mining activities with the integrity of nature. However, traditional ore mining and processing thus far has shown to considerably affect the environment.

Based on experimental work conducted at TU Bergakademie Freiberg, an approach is proposed which can be developed into an applicable process technology that makes use of the capability of supercritical carbon dioxide (scCO₂) to stimulate low-permeability rock. One advantage of scCO₂ compared to water is the lower viscosity enabling scCO₂ to enter hairline fissures and disintegrate siliceous, oxidic or sulphidic species and to transform them into the respective carbonates. Carbonates will not react with supercritical carbon dioxide; however, this changes when water is mixed with carbon dioxide, because then the acidic water dissolves carbonates. In this respect the treatment is comparable to natural weathering and karstification. The carbonation of e.g. feldspars is accompanied by volume reduction thereby producing additional pathways for the supercritical gas to migrate through fissures generating an enhanced reaction surface for CO₂ to interact with the mineral species of interest.

The proposed technology is of particular interest for low-grade deposits. The enhanced *in-situ* ore processing will dispense with traditional underground mining methods for hard rock applications, replacing them with a new method using drilling operations. The excavation process will apply a combination of supercritical carbon dioxide for fracturing and stimulating and carbon dioxide water mixtures for leaching the metal component in the underground is a new ore-processing technology. Chemical treatment of the produced suspension is easier because lode matter needs no separation on the one side and small ore particles that do not dissolve will be separated easily from the suspension by floatation on the other side. FeCO₃ and CaCO₃ can be fractionated and precipitated and sold as by-product. After depressurizing the suspension the degassing CO₂ will be compressed and re-injected. Thus no CO₂ will be emitted.

This technique can be applied for greater depths and also for those ore bodies that are so far evaluated as being non-mineable. Furthermore, this technique does not impact the environment and is without risk and dirty working environments for workers. The overall objective is to develop an innovative clean and resource-efficient mineral processing route and technology for a better utilization of mineral raw material. This clean intelligent underground processing technology will be a jump ahead in the mining industry, speeding up productivity, because metal separation takes place *in situ* and thus transport of process volumes and waste is minimized. It constitutes a novel technology for the processing of low-concentration ores with removal of impurities and allows for the recovery of base and precious metals, including critical raw materials¹ like rare earth elements (REE). The proposed technology is a closed-process system with non-toxic reagents with zero adverse impact on existing surroundings. Mobile mineral processing plants may come into use.

The vast majority of the earth crust material is characterized by low-permeability rocks with only few fissures and voids. Thus an important step for utilizing the proposed underground ore-processing technology is to increase the permeability of the rocks. For decades stimulation techniques based on either thermal stress or hydraulic fracturing using water have been standard in oil and gas exploration. Gas-fracturing was applied only related to the use of explosives resulting in high but short-lasting gas pressure. In this research, for the first time supercritical CO₂ (scCO₂) is proposed to increase rock permeability. scCO₂ has the advantage of a lower dynamic viscosity and the ability to react directly with feldspars in granite and gneisses (carbonization). Carbon dioxide mixed with water is able to dissolve carbonates and thus to increase permeability and leach the desired trace elements including REE.

The critical point of carbon dioxide (31.1°C, 7.38 MPa) requires, under normal geothermal gradient, depths of about 1 km to be well above the critical temperature. The scCO₂ fracturing technology in combination with CO₂/water extraction has to be investigated and developed as *in-situ* ore processing with representative examples of different types of rocks and deposits. *In-situ* fracturing with scCO₂ has

¹ http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm

not been performed until now; it will be the first time ever. The combination is a completely new extraction technology and therefore offers certain challenges. The research activities comprise a holistic approach covering geological, mineralogical, chemical, and geophysical investigations at different scales (lab to field scale) and characterization of the mining sites, mine design, mining methods and technology as well as modeling aspects. It includes the improvement of (deep) drilling technologies in different types of rocks, further development of logging while drilling technologies, monitoring of seismicity during fracturing experiments, and CO₂ monitoring at the surface of the test site.

A very important point is modeling of the processes at different scales. The models will be utilized both as tool to design the experiments before being performed and after the experiment to evaluate and interpret the results, and eventually improve the model by re-coding. This data will then be used to establish a model of the underground site with the aim to identify through simulation experiments ideal working parameters.

Assuming that a circulation of 10 l/s will be achieved and the solution contains 5 valuable metals at concentrations of 1 ppm, this sums up to 50 g/m³ and thus 4.32 kg per day. Estimating an average price of 3000 to 8000 € per kg this would result in 12960 to 34560 € value add per day (4.73 to 12.61 million € per year, respectively). At the very moment only rough estimations about the investment and running costs are available. But it is rather likely to produce well beyond the costs of conventional mining plus aboveground processing because costs for labor work are significantly lower.

2. Method

The objective of this paper is to study the physical and chemical impact of CO₂ on carbonate rock as a minable ore reservoir for e.g. rare earth elements through numerical simulations using TOUGHREACT. This code is a non-isothermal reactive geochemical transport model, developed by Xu and Pruess. It was established by introducing reactive geochemistry into the multi-phase fluid and heat flow code TOUGH2 (Pruess, 1991; Pruess et al. 1999). The most recent version of TOUGHREACT provides several EOS (equation-of-state) modules:

EOS1 for waters in hydrothermal systems,

EOS2 for multiphase mixtures of water and CO₂ in hydrothermal systems,

EOS3 for multiphase mixtures of water and air (applications to vadose zone and nuclear waste disposal problems),

EOS4 is similar to EOS3 but covers vapor pressure lowering effects due to capillary pressure,

EOS7 deals with multiphase mixtures of water, brine, and air with density and viscosity effects of salinity (extension of EOS3),

EOS9 is based on Richards' equation and is suited for ambient temperature and pressure reactive geochemical transport problems,

ECO2N for multiphase mixtures of water, CO₂ and NaCl (XU et al. 2012).

The ECO2N EOS was created for CO₂ disposal in deep brine aquifers to simulate fluid flow induced by CO₂ injection into deep aquifers (Pruess and Garcia 2001). ECO2 provides an accurate description of the thermophysical properties of mixtures of water and CO₂ at conditions that may typically be encountered in brine formations of interest for CO₂ disposal ($T > 35$ °C; $75 \text{ bars} \leq P \leq 400 \text{ bars}$). For analyzing reactive fluid and chemical interaction with rock minerals induced by CO₂ injection, the reactive geochemistry part of the TOUGHREACT code has been combined with TOUGH2/ECO2, resulting in a new improved reactive geochemical transport simulator TOUGHREACT/ECO2 (Xu et al. 2003). TOUGHREACT/ECO2 uses a sequential iteration approach.

After solution of the flow equations, the fluid velocities and phase saturations are used for chemical transport simulation. The chemical transport is solved on a component basis. The resulting concentrations obtained from the transport are substituted into the chemical reaction model. The

system of chemical reaction equations is solved on a grid-block basis by Newton-Raphson iteration. The chemical transport and reactions are iteratively solved until convergence (Xu and Pruess 1998).

The simulator can be applied to one-, two-, or three-dimensional porous and fractured media with physical and chemical heterogeneity, and can accommodate any number of chemical species present in liquid, gas and solid phases. A wide range of subsurface thermo-physical-chemical processes is considered. The major processes considered for fluid and heat flow are: (i) fluid flow in liquid and gas phases under pressure and gravity forces, (ii) capillary pressure effects for the liquid phase, and (iii) heat flow by conduction, convection and diffusion. Transport of aqueous and gaseous species by advection and molecular diffusion is considered in both liquid and gas phases (Xu et al. 2004).

Temporal changes in porosity and permeability due to mineral dissolution and precipitation can modify fluid flow. This feedback between transport and chemistry can be important and can be considered in the model, but a rather large computational penalty has to be paid if this is modeled explicitly. Alternatively, the model can monitor changes in porosity and permeability during the simulation from changes in mineral volume fractions without feedback to the fluid flow. Changes in porosity during the simulation are calculated from changes in mineral volume fractions. A simple Kozeny- Carman grain model based on spheres is used to calculate changes in permeability due to changes in porosity (Bolton et al. 1999). The Kozeny-Carman equation relates the permeability k (in m^2) to the porosity (ϕ) by

$$k = \frac{R_0^2}{45} \left(\frac{\phi^3}{(1-\phi)^2} \right) \quad (1)$$

where R_0 is the initial local spherical close pack radius. Based on Eq. (1), the ratio of the permeability k to initial permeability k_0 can be expressed as

$$\frac{k}{k_0} = \left(\frac{\phi}{\phi_0} \right)^3 \left(\frac{1-\phi_0}{1-\phi} \right)^2 \quad (2)$$

where ϕ_0 is the initial porosity. The porosity-permeability correlation in geologic media depends on a complex interplay of many factors, like pore size distribution, pore shapes, and connectivity (Verma and Pruess, 1988). Additional porosity-permeability relationships are said to be considered in future. Figure 1 shows the flow chart for solving coupled non-isothermal multiphase fluid flow, solute transport and reactive geochemistry in TOUGHREACT.

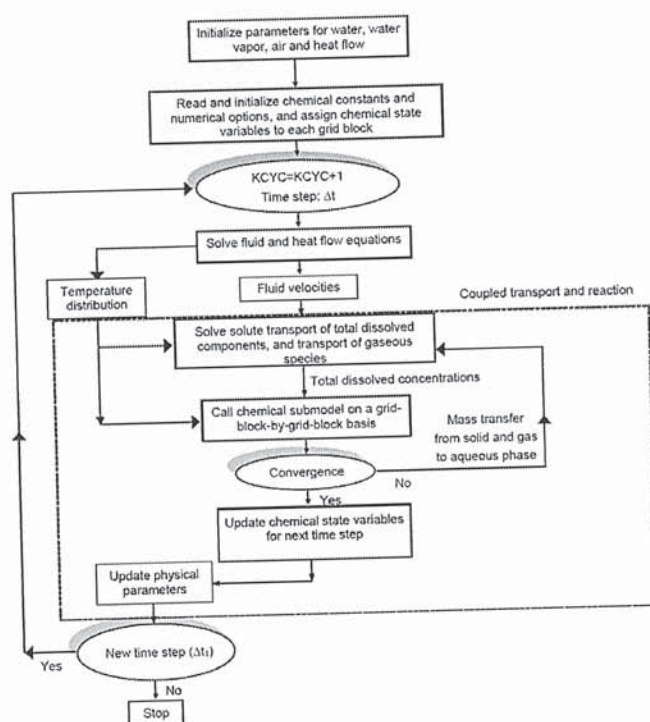


Fig. 1: Flow chart of TOUGHREACT (from Xu et al. 2012)

Space discretization in TOUGH2 and the transport code TOUGHREACT is realized by means of the same integral finite differences (Narasimhan and Witherspoon, 1976) because flow and transport equation have the same structure. The IFD discretization approach and the definition of the geometric parameters are shown in Figure 2. Of course it is as well possible to use any “normal” rectangular finite grid discretization scheme.

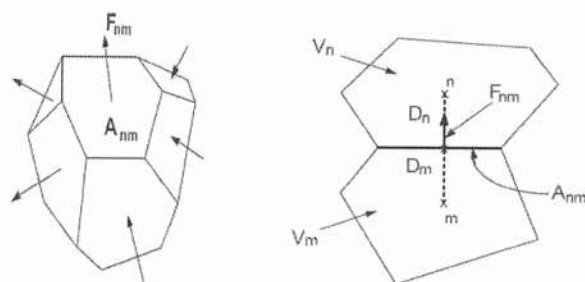


Fig. 2: Discretization scheme and geometric data according to the integral finite difference scheme (from Xu et al. 2012)

3. Limitations

In the present version of TOUGHREACT, the following processes are neglected: (i) compaction and thermal mechanics, such as micro-fracturing by thermal stress and hydro-fracturing by thermal expansion of pore fluids; (ii) effects of chemical concentration changes on fluid thermophysical properties like density and viscosity, which otherwise primarily depend on pressure and temperature; and (iii) the enthalpy change due to chemical reactions. Also TOUGHREACT presently does not have the capability of incorporating solid solutions and pressure dependency of chemical reactions (XU et al. 2012).

Furthermore, in comparison to PHAST (Parkhurst et al. 2010) where the geochemical modeling is based on PHREEQC, TOUGHREACT offers a fairly limited database. However, a tool is available to import a PHREEQC or EQ3/EQ6 database. More critical is that TOUGHREACT computes activity coefficients of charged aqueous species and water by means of the HKF model (extended Debye-Hückel model presented by Helgeson et al. (1981)) which assumes that sodium and chloride are the dominant ions. Another shortcoming is that TOUGHREACT does not offer models based on specific ion interaction theory (SIT, PITZER) which is recommended for water with ionic strength larger than 0.7 mol/l.

4. Model Setup

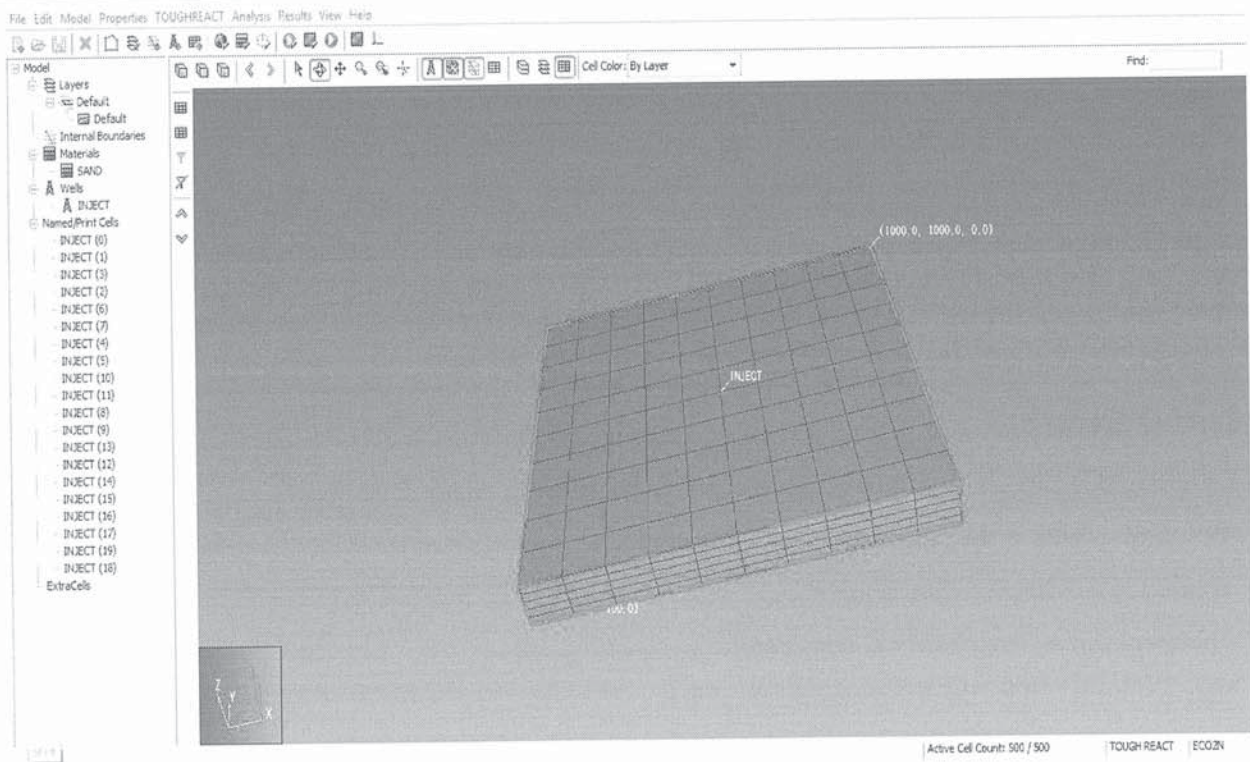
A TOUGHREACT simulation requires four input files. These files are listed below:

- flow.inp -- This is the standard TOUGH2 input file
- solute.inp -- The chemical analysis
- chemical.inp -- The chemical parameters
- thermodb.txt -- The thermodynamic database

To rapidly develop the model and view results, the PetraSim graphical user interface is used to develop a three-dimensional model. PetraSim is an interactive pre-processor and post-processor for the TOUGH family of codes. The carbonate rock ore reservoir is considered as single layer (no gravitational effect) with a thickness of 100 m and dimensions of 1 km in X and Y direction. Grid cells are defined as 100m x 100m x 20m resulting in a total of 500 grid cells. The injection well is placed at the center of the ore layer (500m, 500m) with a length of 100m (Figure 3). The hydrogeological parameters used in the simulation are shown in table 1. Parameters controlling the kinetic rate law for dissolution and precipitation of minerals are taken from literature.

Tab 1: Hydrogeologic parameters for the simulation

Layer thickness	100 m
Permeability	10^{-13} m^2
Porosity	0.12
Compressibility	$1 \times 10^{-8} \text{ Pa}^{-1}$
Temperature	40 °C
Pressure	100 bar
CO ₂ injection rate	70 kg/s
Relative permeability	
Liquid (van Genuchten, 1980):	
$k_{rl} = \sqrt{S^*} \left\{ 1 - \left(1 - [S^*]^{1/m} \right)^2 \right\}^2$	$S^* = (S_l - S_{lr}) / (1 - S_{lr})$
irreducible water saturation exponent	$S_{lr} = 0.00$ $m = 0.457$
Gas (Corey, 1954):	
$k_{rg} = (1 - S')^2 (1 - S'^2)$	$S' = (S_l - S_{lr}) / (S_l - S_{lr} - S_{gr})$
irreducible gas saturation	$S_{gr} = 0.05$
Capillary pressure	
(Van Genuchten 1980):	
$P_{cap} = -P_0 ([S^*]^{-1/m} - 1)^{1-m}$	$S^* = (S_l - S_{lr}) / (1 - S_{lr})$
irreducible water saturation exponent	$S_{lr} = 0.00$
strength coefficient	$m = 0.457$ $P_0 = 19.61 \text{ kPa}$

**Fig. 3: Carbonate rock layer size and grid layout**

As supercritical CO₂ is injected in the carbonate rock layer it reacts with the present water and forms carbonic acid.



Dissociation of carbonic acid leads to the formation of hydrogen carbonate ions



This reaction gives an acid solution (pH close to 4.6) that has the potential to react with minerals in the rock formation (carbonates, salts, etc.) The most reactive mineral is calcite:



5. Results

With a constant injection of scCO₂ at a rate of 70kg/s for a period of 70 days the pressure inside the well and around the well increases from the initial 2×10^7 Pa to 5×10^7 Pa (Figure 4). Carbonic acid with a pH of 4.6 (Figure 5) forms when the injected scCO₂ mixes with the present water and calcite dissolution occurs. Figure 6 clearly shows that significant dissolution of calcite occurs in the vicinity of the well due to carbonic acid presence.

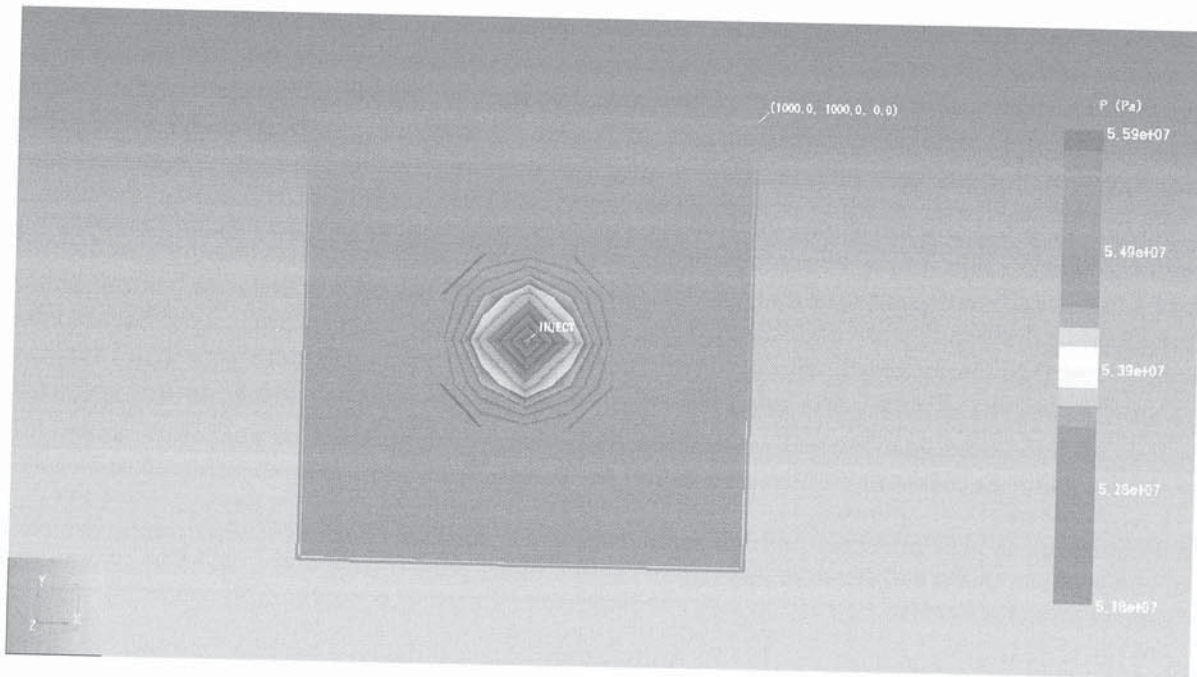


Fig. 4: Pressure around the injection well after 70 days of scCO₂ injection at a rate of 70kg/s. Initial injection pressure is 2×10^7 Pa.

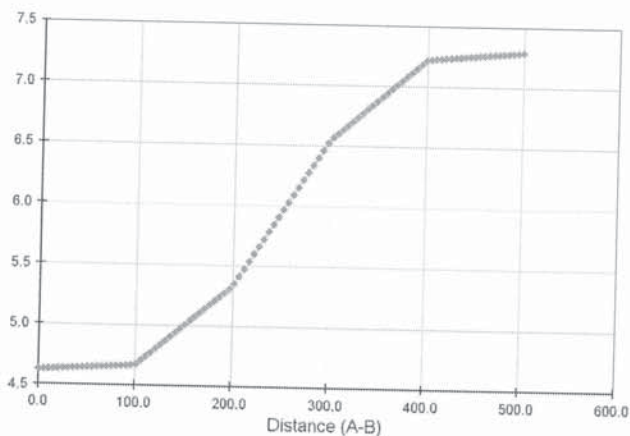


Fig. 5: pH around the injection well after 70 days of scCO₂ injection

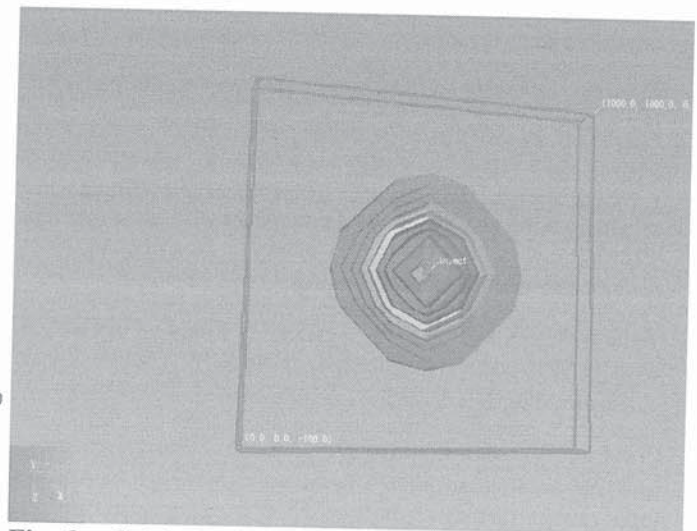


Fig. 6: Calcite dissolution around the well after 70 days of scCO₂ injection

6. Conclusions

A three-dimensional simulation using the TOUGHREACT reactive transport code was used to investigate the use of supercritical carbon dioxide for the extraction of deep ore bodies. scCO_2 was injected into a deep carbonate layer at a rate of 70kg/s for a period of 70 days.

Carbonic acid was formed when scCO_2 mixed with the present water and as a result calcite dissolution occurred. In turn, the dissolution of calcite will create voids and increase porosity. Even a small increase in porosity has a significant effect on permeability enhancement.

During scCO_2 injection, the existing water in the ore layer especially around the well was dried out due to high injection pressure. Hence, the next stage of enhanced in-situ leaching is to pump pure CO_2 into the chemically induces voids and then pump water to mix with the scCO_2 which is present in the carbonate layer.

With the injection of scCO_2 pressure inside the layer increased significantly. This may lead to opening up existing fissures and also creating new ones which in turn will further enhance porosity and permeability. Further geo-mechanical studies are needed to examine the exact response of the ore reservoir to supercritical fluid induced pressure.

This study implies that the new proposed method of in-situ mineral extraction by means of scCO_2 has great potential to become the future technology of mining.

7. References

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