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Potential Subsurface Impacts of CO₂ Stream Impurities on Geologic Carbon Storage

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Abstract

A key impediment to carbon capture and storage is the cost of CO₂ capture, particularly for conventional power plants whose flue gas is dominated by gases other than CO₂. Waste-gas streams from power plants that use novel technologies (such as oxyfuel, the focus of this paper) can circumvent the capture step thanks to their CO₂-rich composition (CO₂>90%), but at the expense of stream CO₂ purity (N₂, O₂, Ar, and other minor species may be present). Relatively high purity levels must be achieved to avoid compression and complications in pipeline transportation (two-phase flow) and, potentially, subsurface impacts. The CO₂ Capture Project Phase 3 (CCP3) has started investigating the latter, which, in turn, inform techno-economic assessments of capture and transportation economics. Subsurface impacts of an impure CO₂ stream could be twofold: (1) complicate flow behavior and reduce static capacity because of density and viscosity differences and (2) undermine reservoir and top seal integrity due to reaction with reactive species (O₂, CO, SO_x). Using a range of potential oxyfuel waste-gas compositions, we approached the first issue through a desktop study using the numerical modeling tool. So that we could work with accurate flow parameters, we performed laboratory experiments in order to determine the actual viscosity and density of the mixtures. Information on solubility of these various mixture components in the aqueous phase under various pressure, temperature, and salinity conditions was also collected. An important observation controlling all results of the study was that viscosity and density of mixtures are lower than those of pure CO₂ at the same temperatures and pressures. It follows that a plume of CO₂ with impurities, moving updip with no barrier, will migrate farther from the point of injection but will be trapped through residual saturation sooner than will a plume of pure CO₂. A larger plume means that a larger area must be inspected for leakage pathways, such as faults and wells, but faster trapping means a shorter monitoring period. Equally important is that contrasts of viscosity and density between pure CO₂ and a CO₂ mixture decrease with depth, suggesting that differences in flow behavior and storage capacity are similarly reduced with depth. Whereas flow behavior may impact the whole field, geochemical impacts are more likely to be restricted to the well-bore environment and the near field. Batch experiments conducted in high-pressure, high-temperature autoclaves with rocks immersed in synthetic brine and exposed to supercritical CO₂ with and without admixed O₂ suggest that O₂ may change the geochemistry of subsurface systems in ways that the pure CO₂ case does not. Results of the study, therefore, present the CO₂ project developer with tradeoffs in capacity, pressure evolution, and monitoring scenarios, with additional costs likely more than offset by reduced capture costs.

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1. Introduction

Power generation and industrial processes that have CO₂ as a byproduct seldom produce a pure CO₂ stream. When the CO₂ fraction is low (as is the case of flue gas from conventional power plants), an amine-based capture system that will increase the CO₂ fraction (to >99%) and possibly eliminate most of the impurities is needed. However, when the CO₂ fraction in the waste stream is already high (e.g., oxyfiring or gasification), capture might not be required, depending on the subsurface characteristics of the strata that are to receive the stream and on other local operational factors (compression, transportation not unduly impacted). This paper proposes to explore the impacts of impurities on CO₂ behavior in the subsurface during geological carbon storage (GCS). Impacts can be classified into two types: (1) direct impact on flow behavior and (2) geochemical impact and indirect impacts on flow.

The focus of the study is on the behavior of the flue-gas streams of gas oxy-fired power plants (combustion in ~pure O₂). Impurities in the flue streams include N₂, Ar, O₂, CO (Table 1), and, potentially, H₂, SO_x, NO_x, and other acid species. Depending on the technology used, a range of compositions can be established from a literature review (Table 1). In addition, discussion with industry experts suggests that maximum volume fractions are 15% for N₂ (that is, ~10% molar in a binary mixture), 5% for Ar and O₂, 2% for CO, and 0.15% for SO_x (see Table 2 for densities). Once the impure CO₂ stream is injected into the subsurface, CH₄ and H₂S gases, which are commonly present in brines in a dissolved state in many basins, can form a significant percentage of the mixture as they partition from the brine into the supercritical phase ([1], [2]). This phenomenon can occur even if the injected stream is composed of only pure CO₂. At this point, a comparison between density and viscosity of the main mixture components could be helpful because they vary with depth. In the subsurface, temperature and pressure are positively correlated, and an exploration of the entire P, T space (Fig. 1) is not needed. Pressure can be assumed to be hydrostatic, and the temperature gradient varies within a relatively small range (15–35°C/km). Density values of all impurities are significantly less than that of CO₂ by at least a factor of 2, with CO₂>>Ar>O₂>N₂>CH₄. Viscosity values follow the same pattern below the depth at which CO₂ mixtures are supercritical.

If impurities can have a plume-wide impact because of changes in flow properties, geochemical reactions are more likely to impact the near-field, where reactive species can be consumed. Reactive gases potentially include O₂, CO, SO_x, NO_x, and minor acid species such as HCl, HCN, and NH₃. Rock-mineral components can dissolve, possibly increasing porosity, permeability, and injectivity, but also compromising the stability of the well. Conversely, neoformed minerals can precipitate and impede flow by decreasing permeability.

Table 1. Molar compositions of oxygas-fired pilot tests from selected references [3][4][5][6].

	Maximum Composition (%)	Minimum Composition (%)	Average Composition (%)	Median Composition (%)
Ar	5.761	0.950	2.546	1.350
CO	0.030	0.030	0.030	0.030
CO ₂	96.200	86.469	92.989	93.278
N ₂	4.508	0.330	2.422	1.900
NO	0.160	0.010	0.063	0.020
O ₂	4.000	0.570	2.605	2.767
SO ₂	0.760	0.100	0.430	0.430

Table 2. Molar composition of base cases (independent of P, T conditions unlike volume fraction).

Component (mol %)	Neat CO ₂	Stream A	Stream C	Single component density at 1 atm and 21°C (kg/m ³)
CO ₂	100	96	92	1.834
N ₂	—	0.2	1	1.161
O ₂	—	2.1	6.5	1.327
Ar	—	1.7	0.5	1.654
CO	—	—	—	1.162

2. Methodology

In this section we describe our approach to the numerical experiments involving flow and geochemical impacts, as well as to independently accomplished autoclave experiments. First, we estimated static capacity, which is especially relevant to the case of structural traps because it relates to the volume occupied by the mixture in the subsurface. Comparison of densities as a function of depth allows for a first-order comparison of capacities. Second, we examined dynamic capacity.

2.1. Dynamic Capacity and Numerical Flow Experiments

In order to focus on the processes of interest and not on specificities associated with an actual site, we developed a generic sloping aquifer and compared results of runs carried out using various CO₂ mixtures. Runs were performed using the CMG-GEM and CMG-WINPROP software packages. GEM is a compositional multiphase flow code that can accommodate multiple gas components and their interaction with a liquid phase. WINPROP is an allied module useful in determining and tuning equations of state. To take advantage of these compositional features, we used the “oil” phase in GEM internally to model the aqueous phase so that the Peng-Robinson equation-of state (EOS) formalism could be used for flash calculations. Because of the lack of accurate data on viscosity and density, we performed 10 experiments (through an external vendor based in Houston, Texas) to tune EOS parameters for various CO₂ mixtures (incorporating CO₂, N₂, O₂, and Ar) at various temperatures (60, 80, and 100°C) and pressures (13.8, 27.6, and 41.4 MPa). We also developed binary interaction coefficients between components under a range of pressure (10–50 MPa), temperature (30–120°C), and salinity (0–200,000 mg/L) conditions through a comprehensive literature audit so as to model dissolution of the mixtures into the brine.

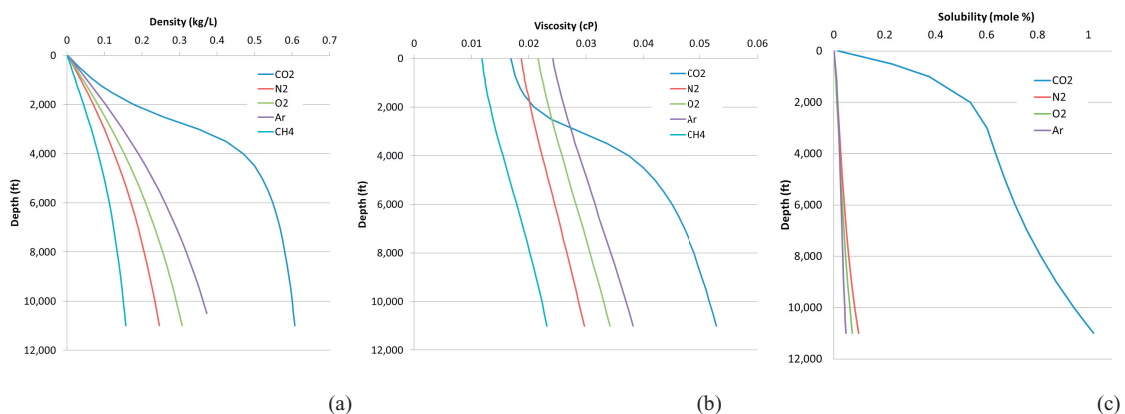


Fig. 1. Density (a), viscosity (b), and solubility (at 100,000 mg/L) (c) of a pure component as a function of depth (hydrostatic pressure and geothermal gradient of 22°C/km) (12,000 ft = 3650 m) (SO₂ would have an opposite impact).

The general approach consisted of a parametric study and sensitivity analyses of a generic case and of three previously studied sites (two on the U.S. Gulf Coast and one in Alberta, Canada), modified slightly to meet our objectives. We initially used a simple dual generic model: a shallow model reproducing conditions present at the Frio site [7][8] and a deep model reproducing conditions prevailing at Cranfield [9][10]. Both sites are on the U.S. Gulf Coast, but for analysis they were stripped of specific properties, retaining only environmental conditions: pressure, temperature, and salinity (Table 3). The only trapping mechanisms simulated in the model were dissolution and residual-phase mechanisms. Mineral-phase trapping on a meaningful scale is generally understood to require at least hundreds or thousands of years. Structural trapping—that is, trapping of CO_2 as would occur in oil and gas accumulations—was not included in the design of the generic model because structural trapping would be of negligible utility in explaining the interplay of all processes and is site specific. The model was large enough (11 km) for the CO_2 mixtures to be fully trapped as residual saturation before reaching the updip boundary, assuming an injection rate equivalent to 0.5 million tons of pure CO_2 for 30 years. Injection occurred at the downdip section of the lower third of the 300-m-thick reservoir (Fig. 2). Results are to be understood relative to one another, in particular relative to the base cases, because of numerical and gridding issues. For example, in homogeneous models, plume extent is a function partly of cell size but mostly of cell height [11]. Scaling the plume extent from various runs to the pure CO_2 base case minimizes this effect.

Table 3. Characteristics of shallow and deep generic models.

Reservoir Property	Shallow Reservoir Case	Deep Reservoir Case
Model dimensions	$11,000 \times 4660 \times 300 \text{ m}^3$	same
Number of cells $x \times y \times z$	$120 \times 51 \times 20$	same
Cell dimensions	$90 \times 90 \times 15 \text{ m}^3$	same
Dip in x direction	2°	same
Permeability /kv/kh / porosity	300 md / 0.01 / 0.25	same
Depth at top downdip	1675 m	3040 m
Initial pressure (equilibrium at time 0)	V.E. ~17.6 MPa at top downdip	V.E. ~32.4 MPa at top downdip
Temperature	135°F	257°F
Injection rate and period	8.5 m^3/s for 30 years	same
Maximum res. saturation	0.30	same
Boundary	No flow except updip (hydrostatic)	
Formation water TDS	~100,000 mg/L	~170,000 mg/L
Simulation period	100 yr	same

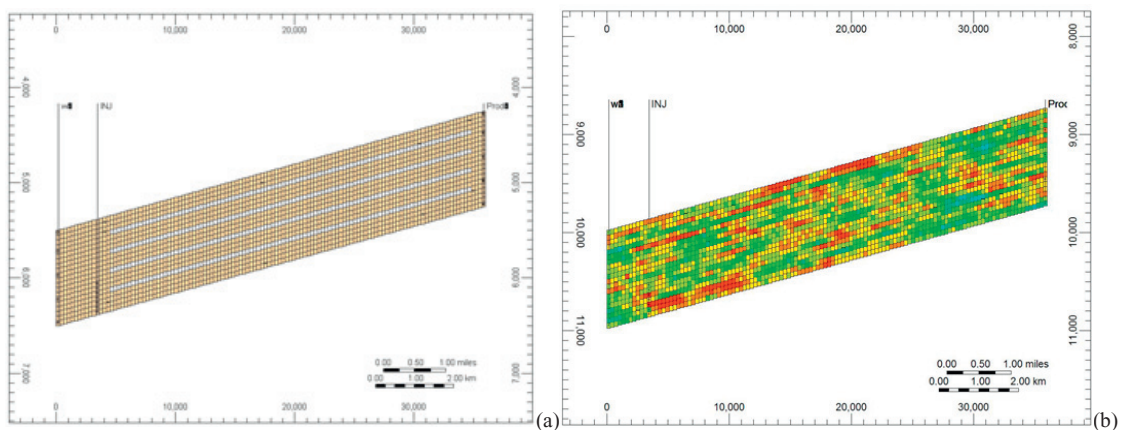


Fig. 2. Cross section of generic model displaying homogeneous field with baffles (a) and heterogeneous permeability field (b).

The metrics used to measure impact on GCS consisted of (1) time for the plume to reach the top and, more important, (2) extent of the plume at a given time or when all of the injected CO₂ mixture had been immobilized, and (3) time until all CO₂ mixture was immobilized. After treating the homogeneous case, we developed reservoir models encompassing a range of heterogeneity: (1) we handled heterogeneity in a simplistic way by adding four baffles with null porosity, parallel to the formation top and bottom, just upstream of the injection well and short of a few cells, all the way up to the updip boundary and across the whole width of the model (Fig. 2a); (2) we obtained multiple heterogeneous fields through permeability generators (Fig. 2b); and (3) we used models from actual sites. We also assessed changes in pH and Eh using the software PHREEQC so as to investigate concentration levels at which minor species could have an impact on the system reactivity.

2.2. Batch Autoclave Experiments

We conducted batch autoclave experiments using pure CO₂ and CO₂:O₂ (~98:2 mol%). The objective of the experiment was to document changes due to CO₂ but, more important, to emphasize differences between the pure CO₂ and the mixed CO₂:O₂ cases. An extensive review of the subsurface behavior of reactive impurities in a CO₂ stream demonstrated that O₂ behavior was poorly known; therefore, O₂ behavior became the focus of the study. Detailed pre- and postreaction water chemistry and rock petrographic, petrophysical, and chemical analyses were used to document alteration (SEM and XRD). Experiments were conducted at different temperatures (75, 100, 130°C), pressure was 200 bars, and we used a 1.88-M NaCl brine (~100,000 ppm) and ~7 grams of rock. Sandstone samples, which were from the U.S. Gulf Coast and Alberta, Canada, consisted of (1) a very fine sandstone with carbonate fragments and feldspars, (2) a sandstone with clay minerals and a small percentage of feldspars and siderite, and (3) a sandstone with abundant chlorite and feldspars. We did not investigate impact on seals.

3. Results

Results are consistent with that of a previous IEAGHG study [12]. Impurities impact static capacity by causing variations in density and viscosity of the CO₂-rich mixture. A lower density impacts CO₂ capacity not only because of the smaller fraction injected and space taken up by impurities, but also because of the generally lower density of the impurities under the same conditions. An approximate proxy for capacity change owing to impurities is provided by the density ratio. The loss of capacity can be >50% at shallow depths (~1000 m, CO₂ and 15% molar N₂) (Fig. 3), but the difference quickly decreases with depth. Similarly, mass injectivity, which measures how much CO₂ can be injected (and which can be represented by the proxy metric of the density:viscosity ratio), also exhibits a value that decreases at shallow depths but recovers with increasing depth.

Dynamic reservoir simulations revealed that, following the pattern of static capacity and for the same reasons, impurities impact CO₂ plume shape (rate of vertical ascent and lateral extent) more markedly at shallow depths where the contrast in density and viscosity with pure CO₂ is at its largest. For example, a 4% mole fraction impurity in a binary system is sufficient to increase plume length in 'shallow' low-dip sloping layers by 25%, whereas a mole fraction of 9 to 15%, depending on the component, is needed to create the same impact in a 'deep' system (Fig. 4). Note that pure-CO₂ plume extent is larger at depth than in the shallow case, but that the difference between streams of pure CO₂ and CO₂ with impurities is smaller in the deep model.

In all cases, plume extent is greater when impurities are present, although residual trapping occurs more rapidly. This is generally the case regardless of reservoir heterogeneity and complexity, although heterogeneity tends to moderate the impact of impurities on plume extent because of the multiplicity of

smaller plumes. Note that heterogeneity tends to increase plume extent because CO_2 favors higher-permeability streaks, but that the contrast between pure CO_2 and CO_2 with impurities is smaller. Overall, a trade-off occurs between larger plume lateral extent owing to the presence of impurities and decreased risk owing to faster trapping (pressure management). Unsurprisingly, change in pH owing to the presence of minor acid species (SO_2 , NO , NO_2 , HCl) compared with a pure CO_2 case depends on the buffering capacities of the rock. The threshold at which pH begins to be impacted is ~ 100 ppm in the unbuffered case and 1000 ppm in the buffered case. An additional change of one unit pH (that is, in addition to that resulting from CO_2) is reached between 0.5 and 1% for the most sensitive species (SO_2).

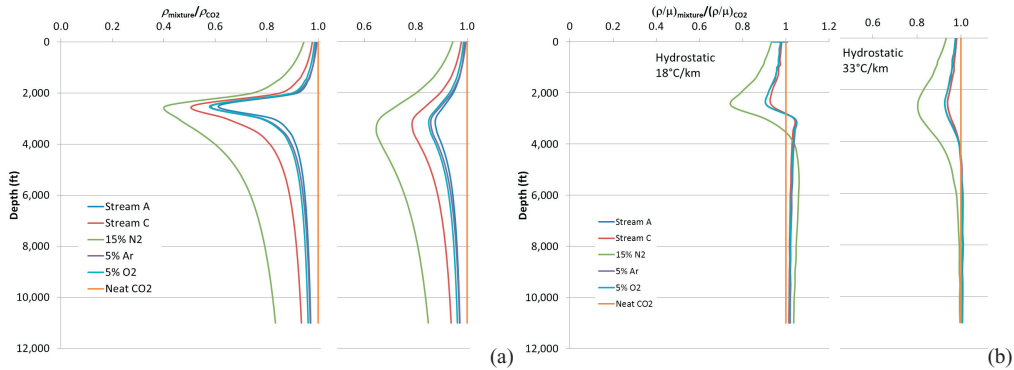


Fig. 3. Mixture density (a) and density to viscosity relative to neat CO_2 (b) as a function of depth; hydrostatic conditions and geothermal gradient of 18°C/km and 33°C/km (12,000 ft – 3650 m).

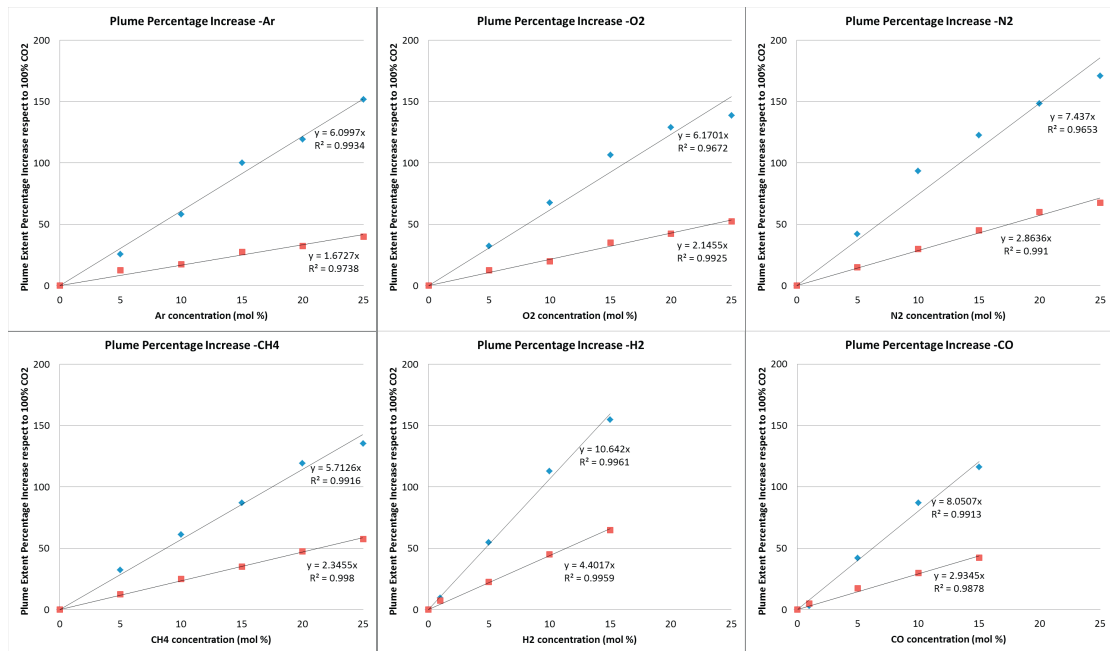


Fig. 4. Plume-extent-increase for binary CO_2 systems compared with pure CO_2 plume extent 100 years after start of injection for N_2 , Ar , O_2 , CH_4 , CO , and H_2 . Horizontal axis represents impurity molar-fraction range (0–25%). Vertical axis displays additional extent; that is, 100% means a doubling of plume length. Linear fitting by forcing straight line through origin.

As expected, rock-water-CO₂ reaction experiments show quick calcite dissolution and slower feldspar dissolution as the two major mineral reactions. Preliminary results of the experiments with and without O₂ show some different reactions for the Alberta sample. Compared with the sample reacted with pure CO₂, the presence of O₂ caused pyrite oxidation and produced iron oxides which precipitated on the surface of reacted rock (Fig. 5). Water chemistry results suggest faster dissolution of carbonate and feldspar minerals when O₂ is present. The latter was also observed on a Gulf Coast sample with very minor pyrite.

Conclusions

In terms of plume shape and extent, the impact of impurities is more marked at shallow depths, where the contrast in density and viscosity with neat CO₂ is the largest, and decreases with depth. Results also suggest a trade-off between plume extent (area of review with risk of CO₂ leakage) and decreased risk owing to faster trapping. A larger plume translates into a larger area to inspect for leakage pathways, such as faults and abandoned wells, but a faster trapping translates into a shorter period of time to monitor the site. Heterogeneities seem to dampen the impact of impurities, but not in all cases. Observations available to date suggests that the impact of O₂ on carbon storage is likely minimal. In the bigger picture, impacts on reservoirs must be balanced against compression costs vs. costs of capture at high purity levels vs. pipeline capacity and construction costs.

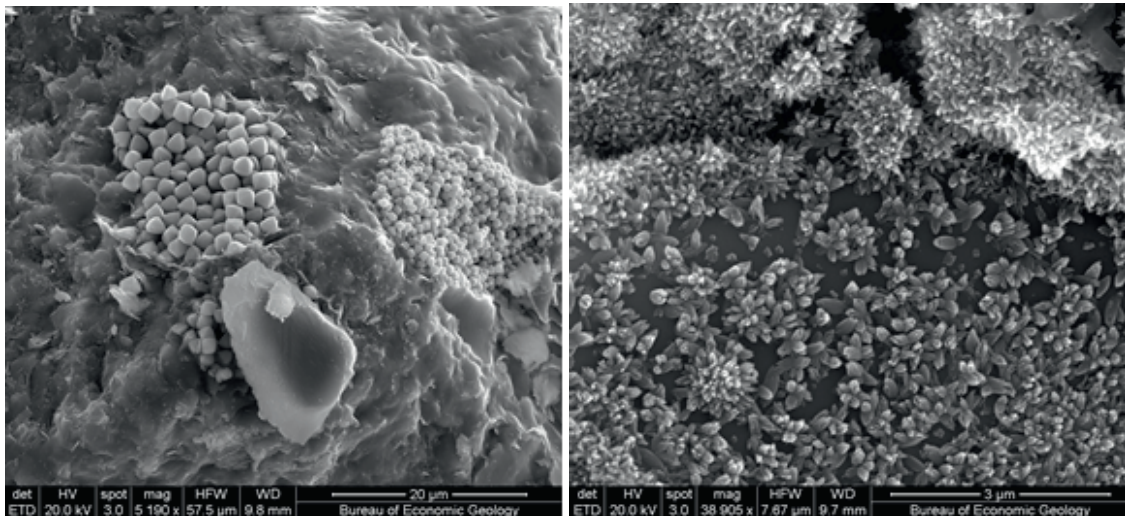


Fig. 5. Unreacted Alberta sample (a): small amount of pyrite present as fresh-looking octahedrons; sample reacted with CO₂ and O₂ (b): quartz grains covered by clusters of iron oxide flakes. Note the scale bar at the bottom right-hand side: 20 μm (a) and 3 μm (b).

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