Application of cross flow ultrafiltration for the determination of colloidal abundances in suboxic ferrous-rich ground waters

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Abstract

A suboxic groundwater from a sandy coastal aquifer was sampled using a new air free, large volume sampling method. Subsequent processing for size fractionation was completed with a modified cross-flow ultrafiltration (CFF) system equipped with a 1 kDa CFF membrane. By purging the CFF system with nitrogen, no oxygen was able to reach the sample. With this optimization, the sample was processed with higher than 90% recovery in terms of both iron and phosphate. The groundwater end member was found to contain only about 4% of the filter passing (< 0.2 µm) iron as colloids and 20% colloidal phosphate. In contrast, if no care is taken to maintain the suboxic environment of the original sample, iron was rapidly and completely oxidized and subsequently lost to the CFF system. Other elements, such as phosphorus measured here, are also lost as a consequence of iron oxidation. This study thus strongly supports the importance of maintaining ambient redox conditions during sampling and fractionation, especially for the determinations of colloid abundances in groundwater.

Keywords: Colloids, groundwater, cross-flow ultrafiltration, iron, redox
Introduction

Groundwater colloids have received increased attention due to their potential role in facilitating the transport of particle reactive elements and/or contaminants (McCarthy and Zachara, 1989). This topic is of great importance to issues related to underground waste storage and drinking water safety. Groundwater colloids can migrate through the porous media similar to if they were dissolved (Ryan and Elimelech, 1996), yet still have a very high inherent binding capacity for many particle reactive elements and organic molecules. The transport rate of these contaminants could therefore be high even if they have a high affinity for the solid stationary matrix (McCarthy and Zachara, 1989). For example, it has been shown that trace elements often are bound to organic colloids in groundwater (Dunnivant et al., 1992; Killey et al., 1984; Mills et al., 1991; Oden et al., 1993). Organic contaminants have also been shown to partition with colloidal organic matter in some studies (Dunnivant et al., 1992). Much attention has been given to colloid-facilitated transport of radionuclides which has been hypothesized as being an important pathway for transport of plutonium at the Nevada Test Site (Buddemeier and Hunt, 1988; Kersting et al., 1999).

When groundwater colloids are sampled in the environment, extreme caution must be paid in both initial groundwater sampling and subsequent colloid separation procedures. The importance of ground water sampling protocols, such as flow rate, pump type and purging time have been emphasized in prior studies (Backhus et al., 1993; McCarthy and Degueldre, 1993; Puls, 1990). The ultimate goal is not to artificially create or mobilize colloids during sampling. In general, the optimum sampling protocol uses a positive displacement pump, such as a bladder pump, using a low flow sampling rate (~
hundreds of mL/min) mimicking the natural groundwater flow. It is recommended that
prior to sampling, one purges the well at low flow rates (micro-purging) until stable
values for turbidity, DO, pH, conductivity and temperature are obtained (Puls, 1990).

Once collected, size fractionation methods also vary considerably. One advantage
of cross-flow filtration (CFF) for size fractionation studies in environmental settings is
that large volume samples can be readily processed (10-100’s liters) to determine colloid
abundances of elements found at even the lowest concentration levels. Over the last
decade CFF protocols have been studied and optimized for the size fractionation of
colloids in both marine (Buesseler et al., 1996; Dai et al., 1998; Dai et al., 2001; Guo et
al., 2000; Gustafsson et al., 1996; Larsson et al., 2002; Wen et al., 1996) and fresh waters
(Buffle et al., 1992; Hoffmann et al., 1981; Pham and Garnier, 1998). These studies have
led to protocols designed to improve membrane cutoff calibration, sample mass-balances
and blank controls. CFF has also been applied in groundwater studies to size fractionate
colloidal actinides (Dai et al., 2002; Kersting et al., 1999) and trace elements (Jensen et
al., 1999; Sañudo-Wilhelmy et al., 2002).

A recent study applying low flow rate well sampling and on site CFF with redox
control throughout revealed no significant association of plutonium with colloids in
groundwater at DOE Savannah River Site F-area. These site specific findings do not
support the hypothesis of colloid facilitated transport (Dai et al., 2002). This is in contrast
to conclusions from an earlier study at this site where different sampling and size
fractionation protocols were used (Kaplan et al., 1994). Further investigations will be
needed to show if this lack of a strong plutonium colloid association is common to other
groundwater settings. What is clear from this work is that careful attention needs to be
paid to groundwater sampling and CFF methods if one seeks to understand transport of colloid associated elements in groundwater (Buesseler et al., 2003).

It is well known that the size distribution of colloids in natural waters can easily change due to aging, changes in pH, ionic strength, redox conditions, light or surface exposure (Chen and Buffle, 1996a; Chen and Buffle, 1996b). The processes that can potentially alter the size distribution, include coagulation, adsorption to surfaces, hydrolysis and precipitation.

Many groundwater aquifers are partly or completely depleted of dissolved oxygen (DO) by degradation of organic matter. When DO levels become low, iron oxide reducing bacteria are favored and the aquifer becomes richer in reduced forms of iron. Ferrous iron in such groundwater is easily oxidized when oxygen becomes available (Davison and De Vitre, 1992; Dzombak and Morel, 1990; Emmengger et al., 1998; Ledin et al., 1994). Groundwater samples are thus easily affected by exposure to ambient air during sampling and analysis. Oxidized iron (III) is expected to be rapidly hydrolyzed and form amorphous iron oxides (hydrous ferric oxides). However, direct evidence for the oxidation of iron (II) upon exposure to air during groundwater sampling and biases on CFF processing has not been demonstrated in a natural groundwater setting. This study was designed to evaluate the importance of maintaining ambient redox conditions in assessing the size distribution of metals in groundwater using CFF. In order to maximize the effect, we chose an iron rich aquifer with reducing conditions.
**Materials and Methods**

*Sample collection*

In January and February of 2001, sampling of a reduced, anoxic, ferrous-rich groundwater aquifer was conducted. The sample well is situated at the head of Waquoit Bay, Cape Cod, MA, USA, about a hundred meters above the saltwater intrusion zone. The well is 11.6 m deep, and the well casing is made of PVC with a 1.2 m stainless steel screen. Prior to sample collection, the well was micro-purged at a low flow rate (0.5 L/min) for a total volume of 100 liters. DO was monitored using an YSI-650/600R multi-parameter sonde in a flow-cell and stabilized at 2.3% oxygen saturation. Samples were filtered with an in-line 0.22 µm Millipore cellulose cartridge, and the outlet from the cartridge was plumbed directly to the sample barrel inlet.

A special sampling barrel was developed for the sample collection, transportation and subsequent CFF processing to eliminate exposure. The barrel is a modified “bag-in-a-bottle” from Berghof (Coral Springs, FL, USA) consisting of a Teflon (PTFE) bag in a Polyethylene over pack barrel. The lid was modified to have an inlet port with a closing valve and Teflon tubing inside leading to the bottom of the bag, inside the barrel. Prior to sampling, the acid cleaned bag was purged with nitrogen gas and evacuated three times to remove any oxygen inside and then sealed. To begin collection, a sample line was connected to the barrel inlet and simultaneously the inlet valve was opened. The sample size in the collapsed bag was monitored gravimetrically during collection. When full, the valve was closed and the sample line disconnected simultaneously. CFF began
immediately after the sample was transported back to the laboratory facilities. The elapsed time from collection to CFF processing was approximately 30 minutes.

*Cross-flow Ultrafiltration*

The colloidal fraction is operationally defined here as being material that passes through a 0.2 µm prefilter and is retained by a CFF membrane with a nominal molecular weight cutoff of 1000 Dalton (1 kDa). The material that is retained by the ultrafilter is concentrated in the retentate reservoir, while the material smaller than the ultrafilter cutoff passes through to the permeate. As the fractionation progresses the retentate reservoir becomes more concentrated. The concentration factor (cf) is described by:

\[
\text{cf} = \frac{(\text{permeate volume} + \text{retentate volume})}{\text{retentate volume}} \quad (1)
\]

The abundance of a chemical element in the colloidal fraction is calculated as

\[
[Me]_{\text{col}} = \frac{[Me]_{\text{ret}} - [Me]_{\text{perm}}}{\text{cf}} \quad (2)
\]

which is valid at any point during the fractionation and also on the integrated fractions at the end of a fractionation.

The ability of the membrane to retain a component is defined as the retention coefficient (RC):

\[
RC = 1 - \frac{[Me]_{\text{perm}}}{[Me]_{\text{ret}}} \quad (3)
\]

The mass balance is evaluated by comparing the sum of the colloidal component (eq. 2) and the permeate component with the total filter passing component:

\[
\text{Loss\%} = \frac{[Me]_{\text{tot} < 0.2 \mu m} - ([Me]_{\text{col}} + [Me]_{\text{perm}})}{[Me]_{\text{tot} < 0.2 \mu m}} \times 100 \quad (4)
\]
Our CFF system consists of a 4 L reservoir bottle, re-circulating pump (Flowjet), 1 kDa regenerated cellulose ultrafiltration membrane (0.5 m² surface area, Millipore Pellican 2) with cassette holder (Millipore Pellicon) and the sample barrel with a feed pump (Fig. 1). The entire system was surrounded by a nitrogen purged tent to minimize redox change during the sample processing. CFF was operated with a cross-flow to permeate ratio of 15 to achieve high recovery (Larsson et al., 2002). The cross membrane pressure drop was approximately 0.4 Bar, and the permeate flow rate was approximately 120 mL/min for all experiments.

After the membrane was mounted in the holder, the reservoir was filled with Milli-Q water, which was de-aerated by N₂ purging and the system was enclosed in the N₂ purged tent. After the remaining storage NaOH solution (pH=10) was rinsed from the membrane with the N₂ purged Milli-Q water, the reservoir was drained and filled with 4 L of sample for preconditioning the membrane. Preconditioning was performed by running the recirculating pump until reservoir level was reduced to 1 L and the permeate discarded, upon which a new acid cleaned reservoir was used, and the tent and bottle were purged again with nitrogen gas. The reservoir was then fed with 4 L of sample for a flushing step where both retentate and permeate valves were directed to the waste and reservoir flushed until 1 L remained. The reservoir was filled again to 1.5 L and CFF processing started.

Sample was fed into the reservoir bottle by the feed pump at the same rate as the membrane permeate flow. Separate variable transformers regulated each of the pumps. Subsamples were taken from the retentate and permeate during processing. The processing was stopped when a cf of at least 15 was reached. At that time the permeate
outlet was closed and the retentate recirculated for 15 minutes before the retentate was collected into the retentate reservoir. Any remaining liquid was emptied out and weighed for mass balance calculations. The total permeate sample was also sampled. Between CFF sampling, the system was cleaned sequentially by Q-water, HCl and NaOH (Dai et al, 1998; 2002). The membrane was placed in a pH 10 solution during storage.

Three CFF experiments with samples from the same well were conducted using increasing degrees of redox control, referred to as “no redox control”, “partial redox control” and “full redox control”. The experiment with no redox control in sampling and processing was actually performed last. In the partial redox control experiment, the nitrogen tent around the system was purged, and the CFF reservoir bottle was purged at intervals. In the full redox control experiment, the reservoir bottle was continuously purged throughout the CFF with a modified cap design with the sample barrel being put in a second smaller purge bag to exclude any introduction of air to the system. The nitrogen gas was directed through a wash bottle containing sample water to give the purge gas the same partial pressure of carbon dioxide as the sample. This effort was to maintain the pH of the sample, which may have been impacted by the loss of carbon dioxide from nitrogen purging.

**Calibration of membrane cut-off**

Prior to the application of the CFF, the membrane was calibrated against standards of known molecular weight. The calibration was done using a prefiltered fresh water matrix from Goodwill Pond, Cape Cod, MA, USA. The calibration samples were spiked with fluoresceine tagged 3 kDa and 10 kDa Dextran standards, and with 1.3 kDa Vitamine B12 on separate occasions. The inherent humic fluorescence was also used for
mass balance crosscheck even though the molecular weights of the humic material were not known. The fluorescence of Fluoresceine (Ex 458 nm/Em 540 nm) and humic fluorescence (Ex 350 nm / Em 450 nm) were not interfering.

**Total iron analysis**

Subsamples for iron and phosphate were taken in preacidified bottles (pH~1) to minimize oxidation of the ferrous iron. Total dissolved iron (II + III) was measured in subsamples after reduction using the ferrozine method (Stookey, 1970). In the reduction step, 15 mL samples were incubated at 60 °C for 1 h after addition of 0.2 mL 1 M hydroxylamin hydrochloride and determined by spectroscopy.

**Phosphate analysis**

Phosphate was determined using a Lachat Quick-chem 8000 (Zellweger Analytics) automated ion analyzer. The Lachat method used is 31-115-01-1-H "Measurement of Orthophosphate by Flow Injection Analysis" which is based on a colorimetric flow injection analysis where phosphate reacts with ammonium molybdate and antimony potassium tartrate (pH < 1) to form a blue complex.

**Dynamic light scattering**

A separate experiment was conducted to measure colloid formation rates using dynamic light scattering. Dynamic light scattering, or photon correlation spectroscopy, in batch mode is a minimum-perturbing technique and it was chosen to measure the kinetics and size distribution of colloid formation during initial oxidation of an anoxic groundwater in order to better understand the ultrafiltration data. The instrument (90°, 100 mW, 809 nm laser) used was a PD-2000 DLS from Precision Detectors Inc. (Bellingham, MA, USA). Samples were injected into a gas tight flow-cuvette. The
instrumental conditions were; 10 µs sample time for first point in autocorrelation function, run time for each accumulate 5 s, 50 accumulates averaging. From the scattering autocorrelation function the software calculates a size distribution using the algorithms developed by Lomakin (Braginskaya et al., 1983; Lomakin et al., 1999).

The samples were taken in Winkler type oxygen bottles in the field by standard procedures for sampling DO. In the lab, samples were opened and transferred to a syringe and prefiltered with 0.02 µm pore size syringe filters (Whatman Anotop) to remove any existing particles and large colloids. The sample was thus filtered directly into the flow-cuvette where light scattering measurements started immediately. The prefiltration also served to introduce oxygen to the sample so the oxidation process could be followed in the cuvette.

Dynamic light scattering has the advantage of not perturbing the sample but the disadvantage is that the scattering signal is not only dependent on the abundance of colloids but also their size. Sensitivity of the measurement for small colloids (< 50 nm) is very low and a few large particles could have disproportionately large impact on the results. That was why the samples were prefiltered down to 0.02 µm just prior to being injected into the cuvette.

**Results and Discussion**

*CFF membrane performance*

Presented in Table 1 are the membrane characteristics for the different molecular weight standards represented by RC, retentate and permeate concentrations as well as loss percentages. RCs for both 10 kDa and 3 kDa Dextrans are > 99 %, indicating, in terms of retention good integrity of the CFF membrane used in this study. Note that the mass
balance for Dextran was quite good (loss terms –9% and –4%) indicating no significant contamination of losses of these standard molecules to or from the membranes. However, there was a 40 % loss of Vitamin B12 during the fractionation, which we attributed to sorption to the membrane that was visibly colored by Vitamin B12 after the experiment. The inherent humic fluorescence of the pond water matrix was used for mass balance cross check of natural dissolved organic matter. The humic fluorescence showed a very small loss rate (3 and 2 %).

*Groundwater ultrafiltration.*

In the “no redox control” experiment, the CFF results for iron are shown in Figure 2A. The loss of iron was rapid and the longer the processing continues, the more iron was lost. The fact that there is an increase in the loss term, up to 100 % after a cf of 10, is interpreted as iron being precipitated onto the membrane during the CFF processing while the samples were exposed to air and oxidized. Both precipitation and scavenging can take place with the precipitate formed being an efficient co-precipitation agent for additional iron. It is worth noting that the membrane became so rust colored that it had to be discarded after the no redox control experiment was completed.

The loss of phosphate reached 100 % even faster than Fe (Fig. 2B). The reason that phosphate is reaching a 100 % loss at a lower cf (quicker) than iron is most likely due to 1) differences in their partitioning between truly dissolved and iron rich colloids and 2) different affinity for the fresh precipitates on the membrane.

In the partial redox control experiment a significant decrease in the loss rates of iron was observed as compared to the no redox control condition (Fig. 2C). The loss of iron slowly increases with cf, but was below 20 % even at cf = 15. The quick decrease in
colloidal iron can be interpreted as fast oxidation of reduced iron due to the oxygen initially presents, after which the oxidation process became limited due to the limited oxygen supply. The colloidal iron was about 8 % constantly after cf = 5.

The loss rate for phosphate during the partial redox control experiment was again higher than for iron, and increased from ~ 20 to 50 % during the processing (Fig. 2D). The fraction of phosphate determined to be colloidal was higher than iron and was constant at ~ 20 % after cf = 5. The permeate concentration decreased with increasing cf corresponding to increasing losses. This suggests loss of the permeate to the membrane since any breakthrough of either low or high molecular weight colloids would have resulted in an increase in permeate concentration (Dai et al., 1998). Since the colloidal fraction was relatively constant and the loss rate was increasing, this suggests that precipitates were formed on the membrane rather than a production of iron oxide colloids during the processing. It is possible that the oxidized iron colloids are very reactive and rapidly adsorbing on surfaces or on already formed precipitates (autocatalysis).

In the full redox control experiment, the loss of iron through the CFF process was only 0 ± 5 % (Fig. 2E). The colloidal fraction of iron calculated from the integrated permeate and the retentate from the end of the experiment was 5 %. Note that there was an initial increase in permeate concentration until cf=1.5, which represents 1 L processed from a total volume of 28 L. The reason could be related to the initial secondary conditioning of the membrane after the first conditioning and flush. This small initial increase is negligible for the integrated permeate.

The full redox control experiment revealed colloidal iron to be 5 % of total iron. The same CFF analysis of phosphate found the colloidal fraction to be equal to 25 % of
the total (Fig. 2F). Phosphate also showed higher losses of 21% compared to iron, which was in agreement with the other experiments relative to iron. The ratio of HPO$_4^{2-}_{\text{colloidal}}$ / Fe$_{\text{colloidal}}$ was approximately 0.25 while the HPO$_4^{2-}_{\text{tot}}$ / Fe$_{\text{tot}}$ was about 0.06.

In Figure 3 the permeate iron concentration from the experiment with full redox control is plotted against from the experiment with no redox control. Full redox control permeate concentrations are quite stable and are just below the total iron concentrations of 57 µM. A slight decrease was observed as the fractionation progressed. Samples for the no redox control experiment were stored overnight without redox controls. In this experiment, the total iron concentration had only been reduced from 57 to 50 µM (data not shown), however the first permeate subsamples had an iron concentration around 20 µM. This suggests the sample without redox control had to a large extent formed colloids or microparticulates in solution. Permeate concentrations continued to decrease rapidly throughout the CFF processing. After a cf=10 was achieved, permeate subsamples had no detectable iron left. The decrease in permeate iron concentrations along with observed discoloration of the membrane was interpreted as iron precipitate forming on the membrane during the initial sample processing was became more efficient in precipitating further iron.

*Colloid formation kinetics with dynamic light scattering.*

The light scattering intensity, hydrodynamic diameter distribution and mean diameter for the first hour of oxidation are shown in Figure 4. The scattering intensity indicates a significant 5 to 6 fold increase of colloid abundance. Since the scattering sensitivity depends on the size of the colloids, only qualitative conclusions can be drawn
(Filella et al., 1997). It should also be stressed that the size distribution is only qualitative and the fact that small colloids < 80 nm are not seen follows the light scattering theory. Figure 4 also shows the hydrodynamic diameter distribution mathematically deconvoluted from the light scattering autocorrelation function (Braginskaya et al., 1983). An increase in abundance and a small increase in size could be distinguished. The slight increase in size could also be seen in the mean diameter (Fig. 4), even though the deviation in the data is large. It can be concluded that the oxidation is very rapid (seconds to minutes) and the light scattering data indicates that larger colloids were at least initially formed.

The implication of this interpretation for the ultrafiltration data is that colloids formed by oxidation and possibly hydrolysis are not fully stabilized (e.g. by natural organic matter). Since no increase in colloidal iron was measured with CFF in the experiment without redox control, the formed colloids probably coagulated rapidly into precipitates and onto the ultrafiltration membrane. Alternatively, it could be that the membrane is also serving as a surface catalyst for iron precipitation in that experiment.

Conclusions

This size fractionation study of suboxic groundwater found colloidal fractions of 5 % iron and 20 % phosphate provided full redox controls were followed. Without these precautions, colloidal fractions would otherwise be overestimated as was evident from results found in the no redox control experiment. Results from the partial redox controlled experiment also showed significant errors occurred in the size fractionation of iron and phosphate. It can be concluded from this study that great care must be taken to
maintain the ambient redox conditions for a groundwater sample during collection, transport and fractionation or analysis. Moreover, the oxidation and hydrolysis of iron (II) is not only affecting the size distribution of iron itself, but influenced other elements such as phosphorus shown here, due to its high affinity of iron oxides to adsorb/scavenge other elements. This study indicates the need for similar redox precautions to be applied during sampling and CFF procedures, to avoid artifacts that erroneously affect results and subsequent conclusions regarding colloidal-facilitated transport in groundwater.

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References


Pham, M.K. and Garnier, J.-M., 1998. Distribution of trace elements associated with dissolved compounds (<0.45 µm-1 nm) in freshwaters using coupled (frontal...
Table 1. Calibration of ultrafiltration performance.

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<tr>
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<th>Conc. factor</th>
<th>Retention coefficient</th>
<th>Retentate conc.(^a)</th>
<th>Permeate conc.(^b)</th>
<th>Loss</th>
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<tr>
<td>10 kDa Dextran</td>
<td>99.5 %</td>
<td>2.85 µM</td>
<td>15.5 nM</td>
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<td>(C_0 = 86.5 \text{nM})</td>
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<tr>
<td>3 kDa Dextran</td>
<td>99.6 %</td>
<td>690 nM</td>
<td>2.78 nM</td>
<td>-3.8 %</td>
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<tr>
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<tr>
<td>Vitamine B12</td>
<td>16.9</td>
<td>98.8 %</td>
<td>15.8 µM</td>
<td>0.187 µM</td>
<td>39.9 %</td>
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<td>(1.35 \text{kDa})</td>
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<td>(C_0=1.85 \text{µM})</td>
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\(^a\) Retained by 1kDa membrane

\(^b\) Passed through 1kDa membrane (truly dissolved)

\(^c\) Initial concentration
Figure 1. The cross-flow ultrafiltration system in a nitrogen purged tent including feed and recirculating pumps, membrane and the retentate reservoir. The sampling barrel is in a separate purged tent.

Figure 2. The cross-flow ultrafiltration results shown as percentage colloidal, permeate (< 1 kDa) and loss for; A) iron from the no redox control experiment (C₀ = 50.4 µM), B) the no redox control phosphate results (C₀ = 3.33 µM), C) the iron results for the partial redox control experiment (C₀ = 49.0 µM), D) the partial redox control phosphate results (C₀ = 4.22 µM), E) the iron data of the full redox control experiment (C₀ = 56.7 µM) and F) the full redox control experiment phosphate results (C₀ = 3.36 µM).

Figure 3. The permeate subsample iron concentration is plotted as a function of concentration factor for the experiment with full redox control and the experiment with no redox control.

Figure 4. Dynamic light scattering results showing from top to bottom average particle diameter (nm), the size distribution (logarithmic) and the light scattering intensity.

Sample prefiltered (20 nm) just prior to injection.
Figure 1. Sample CFF-membrane 1 kDa MWCO

- N₂
- Recirc. pump
- CFF-membrane 1 kDa MWCO
- Feed pump
- Retentate reservoir
- Permeate
- Balance
Figure 2.
Figure 3.

- **Permeate iron conc. (µM)**
- **Concentration Factor**
- **Total iron conc.**
- **Full Redox control**
- **No redox control**
Figure 4.