## **Innovative Technology for Selective Contaminant Removal**

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## ABSTRACT

This paper describes a two-stage water treatment technology for removal of dissolved contaminants that is relevant to many water matrices. Removal is achieved by adapting conventional adsorption, coagulation and flocculation, or lime softening and/or soda ash (or pearl ash) protocol as a pre-treatment mixing conditioning step followed by a novel hydrodynamic separation stage. This hydrodynamic separator (HDS) uses centrifugal force to create fluid flow patterns that sweep particles in the transverse direction so that they relocate to either of two neutrally stable force equilibrium positions where they concentrate into a band. By placing a flow splitter at the end of the channel we obtain a clean effluent stream and a concentrated particle stream. Advantages of this technology over conventional practice include: small foot print, low energy requirement, rapid process, and continuous flow operation. Added benefits include no moving parts, high scalability, high modularity in construction, and low cost in materials and TCO. This technology has been tested on many raw water matrices. Results for efficient removal of scaling agents and dissolved hydrocarbons are discussed.

*Keywords*: Hydrodynamic separation, dissolved contaminants, precipitation, adsorption

## **1 INTRODUCTION**

Removal of dissolved contaminants constitutes a big part of water treatment requirements. Different approaches are available, including bacterial digestion, adsorption, and precipitation. The biological treatment process is slow and requires large land space. Adsorption onto activated particle beds or GAC filter cartridges is limited to relatively small surface areas (although the nanoporous surfaces have areas of very many orders of magnitude greater) requiring frequent replacement and down time for back flush and regeneration. Chemical precipitation is achieved by a combination of lime softening and soda ash or pearl ash treatment followed by sedimentation or filtration. This method through conventional means generates high sludge volumes and requires long processing times and large land space.

In this paper, a novel technology is presented that can significantly reduce process time, land space requirement, and minimize regeneration and maintenance time. The Palo Alto Research Center (PARC) has invented, tested and demonstrated at the laboratory scale a novel, low-cost, hydrodynamic separation technology to remove small inorganic and organic particles from multiple water matrices [1-4]. Besides using this technology to remove already existing suspended particles from a liquid stream, it can be used in different ways to address dissolved solids: (1) By using a precipitation step as a first conditioning step, precipitated solids can be removed in a continuous, in-line process stream; (2) Activated carbon beads or other functionalized micro beads can be introduced into the source water stream for absorbing the dissolved contaminants. The hydrodynamic separator is then used to remove these microbeads for reuse and recycling.

In the following sections we provide a more detailed description of this novel separation technology followed by two specific application examples for removal of selected dissolved contaminants.

## 2 HYDRODYNAMIC SEPARATION

An innovative hydrodynamic separator is used to separate suspended solids, including precipitates, in a contiunuous flow process. This hydrodynamic separator (HDS) uses centrifugal force to create transverse fluid flow patterns that generates a combination of drag and lift forces that sweep suspensions to a force equilibrium position near one of the side walls. This use of centrifugal force is different from that in traditional hydrocyclones and centrifuges where particles of different density from the liquid are moved relative to the liquid using very high (1000s) relative centrifugal force (RCF). In contrast, the PARC hydrodynamic separator uses hydrodynamic forces to move suspensions, requiring very low (single digit) RCF. The flow patterns in the separation channel sweep particles in the transverse direction so that they relocate to either of two neutrally stable force equilibrium positions where they concentrate into a band (Fig. 1).

By placing a flow splitter at the end of the channel we obtain a clean effluent stream, and a concentrated particle stream (Fig. 2). The HDS works for particles above a lower cut-off size. This cut-off size depends on channel geometry and flow conditions and can be designed to meet or exceed the cut-off size of 20  $\mu$ m or 50  $\mu$ m depth filters currently in use as pre-filters. Fig. 3 shows separation results of a 10  $\mu$ m cut-off hydrodynamic separator with a 50-50 flow split ratio, which operates at 22.6 W / gallon per hour (gpm). By changing the effluent to waste flow rate ratio to an 80-20 value the energy requirements immediately drops to 17.5 W/gpm while the same effluent flow rate is maintained.



Figure 1: Schematic drawing of separator channel with relevant forces: drag and lift forces move suspended particles to equilibrium positions close to the channel walls. Centrifugal force creates a transverse flow pattern (Dean's vortices), which break the symmetry and force particles to concentrate near one side wall only.



Figure 2: Picture of a demo separator using a carbon bead suspension. Particles enter the separator at the one o'clock position. By the time they reach the ten o'clock position a tight band has formed that is separated off as waste stream by a flow splitter.



Figure 3: Particle size distributions of a water spiked with 5  $\mu$ m and 30  $\mu$ m carbon beads before and after separation.

The novel and innovative capability of this system is its ability to separate particles of any density, including neutrally buoyant particles such as algae and other biological and/or organic matter, from the source water without the use of a physical barrier, thus reducing any system downtime due to clogging and fouling.

This technology has been tested on many raw water matrices, including seawater, produced water, and wastewater. Carbonates and hydroxides have been precipitated and removed from seawater to reduce Ca and Mg. A similar process has been used on produced water with TDS > 170,000 ppm to remove Mg, Ca, Ba, and Sr with efficiencies > 95%. Tests on a produced water sample with dissolved silica of 110 ppm (turbidity of 2110 NTU, TSS=3341 mg/L) reduced the output effluent to a dissolved silica content of 12 ppm (turbidity of 41 NTU, TSS=52 mg/L). Based on test results with our research prototypes and technical analyses conducted to date, the technology appears compelling on a number of dimensions:

- Highly effective with neutrally buoyant materials, making it suitable also for removal of organics as well as oil/water separation.
- Effective at removal of dissolved materials via precipitation and rapid separation; useful for remove scaling materials that create fouling and clogging problems.
- Small footprint with lower energy and higher removal efficiency than most other clarification approaches of similar scale.
- Short process time shorter time to aggregate smaller floc and replacement of sedimentation with hydrodynamic separation.
- Reduction in solids generation the reduction in chemicals, and the avoidance of overdosing are both expected to contribute to overall reduction in solids in approximate proportion to the reduction in chemicals.
- Demonstrated for raw water with high TSS up to several weight %.

## **3** SAMPLE RESULTS

## 3.1 Removal of Scaling Agents

Elevated levels of multi-valent metal ions like Ca, Mg, Ba, and Sr are prevalent pose a distinct challenge for many process waters, since they tend to form scales that can hamper the performance and life time of filters, heat exchangers and other process equipment. Controlled precipitation of these multivalent ions can be achieved e.g. by lime-ash softening. Instead of following up with a time and space consuming sedimentation step the precipitates can be separated using a hydrodynamic seprator. Fig. 4 shows a schematic digram of a process train for removal of dissolved contaminants using a precipitation step followed by a hydrodynamic separator.





#### Figure 4: Process flow diagram.

## **Scalent Precipitation**

Raw Ca (mg/L)	9960
Raw Mg (mg/L)	2700
Residual Ca (mg/L)	10
Residual Mg (mg/L)	37.5
Ca Precipitation Eff (%)	99.9
Mg Precipitation Eff (%)	98.61

Figure 5: Top: Particle size distributions of sample, effluent and waste (concentrate) streams; Bottom: before and after dissolved Ca and Mg content. A typical example for water that suffers from excessive multi-valent metal ion concentration is produced water. To remove these ions we have treated sample produced water by addition of stoichiometric calculated doses of calcium hydroxide and potassium carbonate to form precipitates which were then characterized and run through the hydrodynamic separator. Input and output streams are analyzed for divalent metal content by titration. Fig. 5 shows the particle size distribution where >93% of the precipitates have been removed. The table in Fig. 5 shows before and after dissolved Ca and Mg content with removal efficiencies of 98 to 99%.

# 3.2 Removal of Dissolved Volatile Hydrocarbons

Volatile hydrocarbons such as benzene, toluene, ethyl benzene, and xylene (BTEX) are volatile organic compounds (VOC) from petroleum derivatives that, in being harmful to the central nervous system, warrant removal from water, which is achievable through adsorption onto activated carbon particles (ACP). Fig. 3 shows a prototype hydrodynamic separator removing ACP in the 5 to 30  $\mu$ m size range from the fluid mixture that may contain volatile hydrocarbons. The inlet at the 1 o'clock position shows homogeneously dispersed ACP. Separation is designed to be completed within one 360-degree turn. The two outlets to the left of the inlet are for the waste and effluent streams. The contrast between the dark and clear images of the fluid show the efficiency in recovery of ACP which exceeds 95% and may be further optimized.

ACP dosage calibration studies indicate that 0.2% loading with 10 minutes slow stirring is sufficient to adsorb an initial BTEX concentration of 50 ppm down to < 1 ppm. For the proof of-concept experiments, toluene and xylene are artificially dosed into deionized water at concentrations equivalent to 50 ppm and 123 ppm of EPA VOC Mix 2 (Sigma 48777). After stirring, both samples were run through the hydrodynamic separator and effluent and waste streams collected for TSS, particle size distribution (PSD) and BTEX measurements. The BTEX/TPH RaPID assay (CyberSense) conforms to the EPA approved method 4030, and is based on enzyme linked immuno-sorbant assay (ELISA). It provides a color reaction based on concentration which is read by a spectrophotometer with a quantification range of  $0.09 \rightarrow 3$  ppm. The calibration vials for the spectrophotometer measurements are shown in Fig. 5 with the expected color shift in deceasing BTEX concentration going from left to right in the image.

Fig. 6 shows a possible process train for using an ACP slurry process step for removal of volatile organics. After exposing the source water for sufficient time to the slurry, the carbon particles are removed from the source water using the HDS for reuse and recycling. Example results for particle size distributions from laser scattering measurements of the input sample, effluent, and waste steams are shown in Fig. 7 where >98% recovery efficiency

is achieved for the ACP. The table shows the corresponding BTEX concentrations with two orders of magnitude reduction by adsorption. The 50 ppm and 123 ppm samples show residual concentrations of 0.7 ppm and 1.7 ppm, respectively. Optimization of ACP adsorption conditions will further enhance BTEX removal. At lower concentrations of BTEX, for example, the 24 ppm maximum reported in the literature for North Sea produced waters; proportionally lower residual BTEX concentrations will be possible.



Figure 5: Callibration of ELISA assay to determine

adsorption of BTEX.

Absorption at 450nm quantifies BTEX from 0.09 to 3 ppm



Figure 6: Process flow diagram.



Figure 7: Particle size distributions of effluent and concentrate (waste) stream.

## 4 CONCLUSIONS

This paper has described a two-stage water treatment technology that is relevant to many water matrices. The first mixing-conditioning step may incorporate stage conventional methods to treat dissolved contaminants, i.e. by precipitation or adsorption. The second stage hydrodynamic separation step efficiently removes suspensions through a waste stream without the need for physical filtration. Adsorbents may be recovered for regeneration and reuse. Sample results for removing dissolved VOC, scalants, and dissolved silica show extremely promising performance albeit with research prototypes that have not been tuned for the respective water matrix. This technology has the potential to treat many other types of contaminants. The advantages over conventional practice include: the small foot print, low energy requirement, rapid process, and continuous flow operation. Added benefits include no moving parts, high scalability, high modularity in construction, and low cost in materials and TCO. In addition, this technology can also remove algae and bacteria which have near-neutral buoyancy, as well as perform oil/water and gas/liquid separations.

### REFERENCES

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