Trace Cr(VI) Removal by Weak Base Duolite A-7 and SIR-700 from Groundwater in Glendale, CA : Underlying Mechanism

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Executive Summary

During the last six months, we carried out a series of laboratory experimental studies using two weak-base anion exchange resins: Duolite A-7 from Rohm and Haas Co., and SIR-700 from ResinTech Co. Chromium-contaminated Glendale water, spiked Glendale water and synthetic water were used in the study. For comparison and appropriate understanding of underlying Cr(VI) removal mechanism, a strong-base anion-exchange resin was also included in the investigation. Major conclusions resulting from the study can be summarized as follows:

1. Cr(VI) removal by Duolite A-7 and SIR-700 takes place by selective anion exchange followed by Cr(VI) reduction to Cr(III) which is insoluble and retained within the resin phase.
2. At neutral or above-neutral pH, Cr(VI) removal by Duolite A-7 and SIR-700 diminishes drastically due to the lack of protonated anion exchange sites. At acidic pH, conventional strong-base anion exchange resins exhibit relatively poor removal of Cr(VI) because of their inability to reduce Cr(VI) to Cr(III). Thus, both anion exchange sites and reductive potential are simultaneously needed for an ion exchange resin to achieve efficient Cr(VI) removal. Duolite A-7 as well as SIR-700 satisfy these requirements at slightly acidic pH following adequate protonation of weak-base exchange sites. Also, the process is operationally simple; any fluctuation in the influent Cr(VI) concentration has no noticeable effect on the treated water quality.
3. During lengthy column runs, chromium appearing at the exit of the column is only Cr(VI) i.e., $HCrO_4^-$ and/or CrO_4^{2-}. Cr(III) is essentially absent in the treated water. Inside the exhausted Duolite A-7 and SIR-700, however, only Cr(III) is present.

4. Removal of copper from Glendale water has no favorable impact on Cr(VI) removal. Thus, even in the absence of copper, Cr(VI) removal by Duolite A-7 and SIR-700 is very efficient. However, both Duolite A-7 and SIR-700 have the ability to remove copper(II) and other transition metal cations due to the presence of nitrogen-containing functional groups.
5. All other conditions remaining identical, Cr(VI) removal is enhanced by lower influent pH and longer empty bed contact time (EBCT).
6. During the field trial of SIR-700 by Malcolm Pirnie, it was observed that Cr(VI) removal for the first few thousand bed volumes was relatively poor. Inadequate protonation of SIR-700 was the underlying reason for inefficient Cr(VI) removal. Both Duolite A-7 and SIR-700 should be equilibrated at slightly acidic pH (3-4) prior to starting the column run for Cr(VI) removal.
7. It is hypothesized that repeating organic groups (Phenol formaldehyde in Duolite A-7 and epoxy in SIR-700) are responsible for reducing Cr(VI) and the resulting organic substances are retained within the ion exchange resins following oxidation. More widely used anion exchange resins with polystyrene matrices are unable to reduce Cr(VI).
8. Results of our laboratory experiments and the earlier findings from the field trials performed by Malcolm Pirnie provide suggestive evidence that intraparticle diffusion within the ion exchangers is the rate limiting step for Cr(VI) removal.

Experimental Results and Major Findings

Selected experimental results and their discussion are presented here for elucidation of underlying Cr(VI) removal mechanism by two weak-base anion exchange resins: Duolite A-7 and SIR 700.

EXPERIMENT I.

Two fixed-bed column run experiments were carried out in the laboratory with Glendale, CA GS-3 water at slightly acidic pH where $HCrO_4^-$ is the predominant chromate species. A strong-base anion exchange resin (Purolite A-600) and Duolite A-7 were the two sorbents under identical experimental conditions. Figure 1 provides the chromate effluent histories for the two runs; empty bed contact time (EBCT) and superficial liquid velocity (SLV) are included in Figure 1. Note that chromate removal is well over an order of magnitude lower for the strong-base anion exchange resin compared to Duolite A-7. Previous research studies established that ion exchange is the primary chromate removal mechanism for strong-base anion exchange resins.
Finding: Ion exchange alone cannot be the sole chromate removal mechanism for Duolite A-7. The same conclusion is applicable for SIR 700.

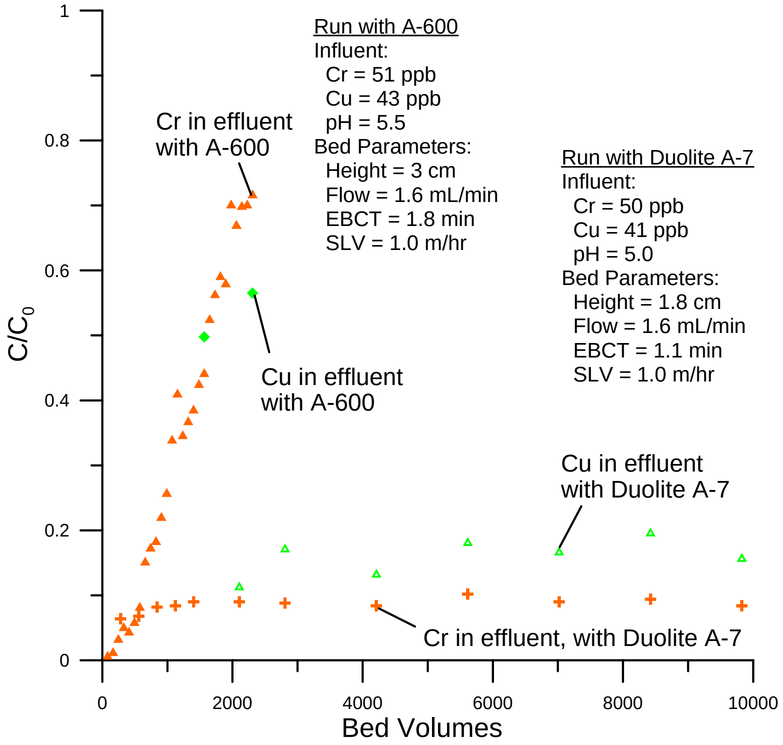

Figure 1. Effluent breakthrough profiles for Glendale well water for strong-base anion exchange (SBA) resin (Purolite, A-600) and weak-base anion exchange(WBA) resin (Duolite, A-7) .

EXPERIMENT II.

It was earlier observed by Malcolm Pirnie that there was a difference between the chromium removal characteristics of SIR-700 and Duolite A-7. Duolite A-7 showed high chromate removal for Glendale water from the very beginning of the run. On the contrary, SIR-700, did not show good removal of chromium for the first 2200 bed volumes but chromate removal improved markedly beyond that point. In our laboratory, SIR 700 was first pre-conditioned with a brine solution with a pH of 3.5 and then fixed-bed column run was carried out with Glendale water. Figure 2 represents chromium breakthrough profile of SIR-700. It may be noted that adequate protonation of WBA resin improves the initial performance of the resin. Also, pre-conditioning of the resin at acidic pH did not cause any significant drop in pH at the exit of the column.

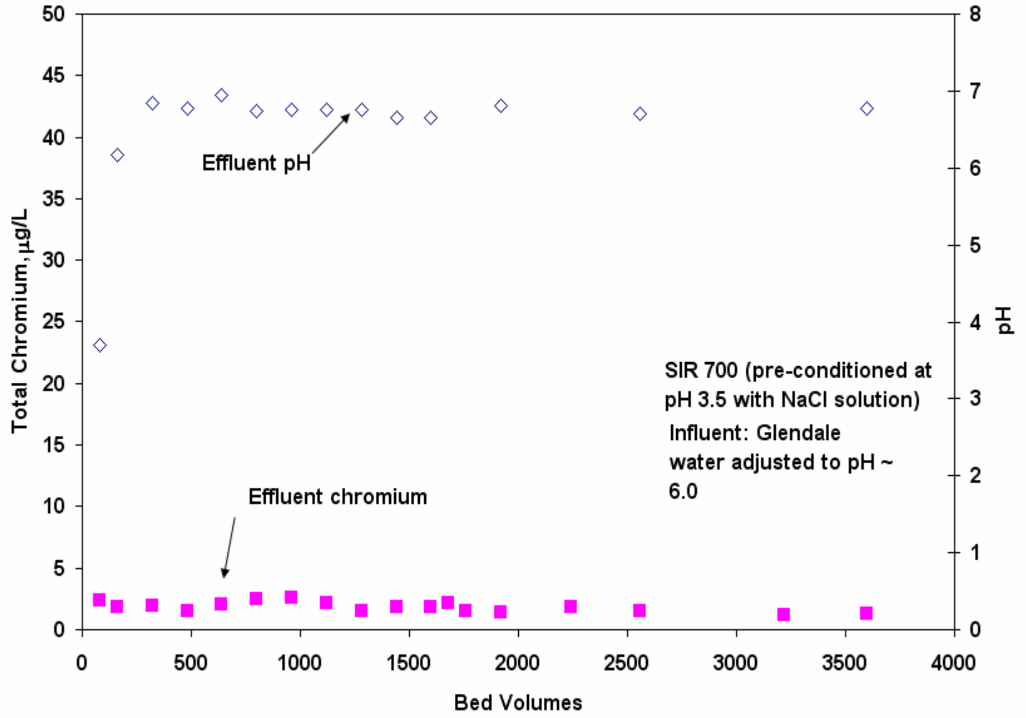

Figure 2. Chromate breakthrough history for WBA resin SIR-700 pre-conditioned with slightly acidic NaCl solution.

EXPERIMENT III

Figures 3 and 4 present effluent chromate breakthrough profiles for two separate column runs: one with parent SIR-700 and the other with copper-preloaded SIR-700 resins. In both cases synthetic water containing about 100-120 ppb chromium (VI) with other background electrolytes was used as the feed. Note that the chromate breakthrough profiles for both the parent and copper loaded resins are very similar. Thus, the presence of copper in the resin phase does not have any noticeable impact towards chromium removal i.e, ligand exchange is not the underlying reason for very high chromate removal capacity of SIR-700. It was observed that copper was simultaneously removed from the Glendale well water by both SIR-700 and Duolite A-7.

Nitrogen-containing chelating functional groups of Duolite A-7 and SIR-700 are responsible for their high sorption affinity toward copper (or other transition metal cations).

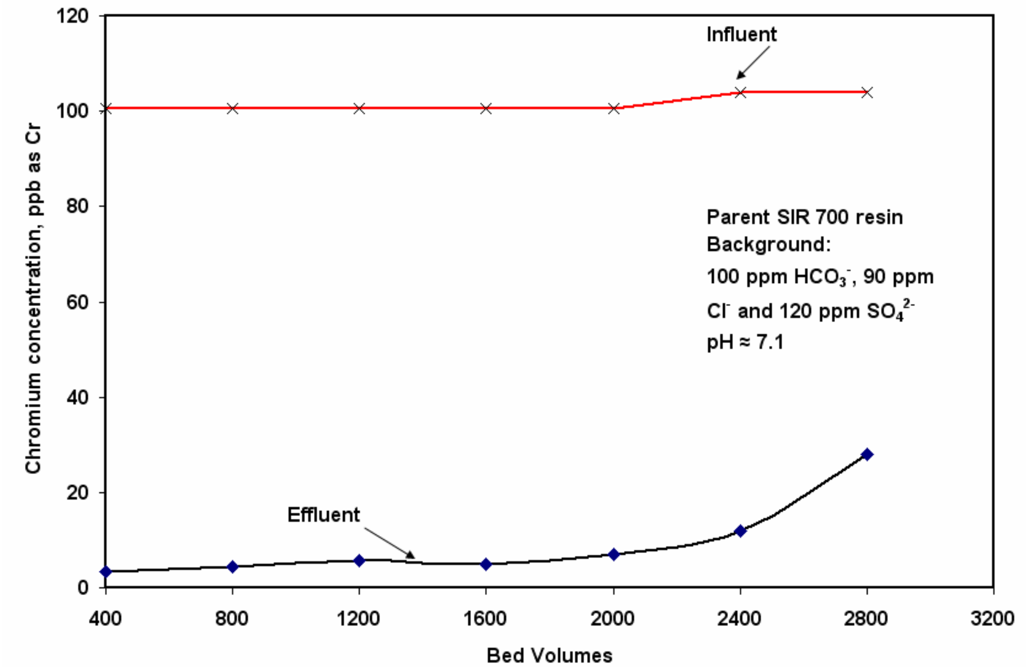

Figure 3. Breakthrough chromate profile for column run with parent SIR-700 resin

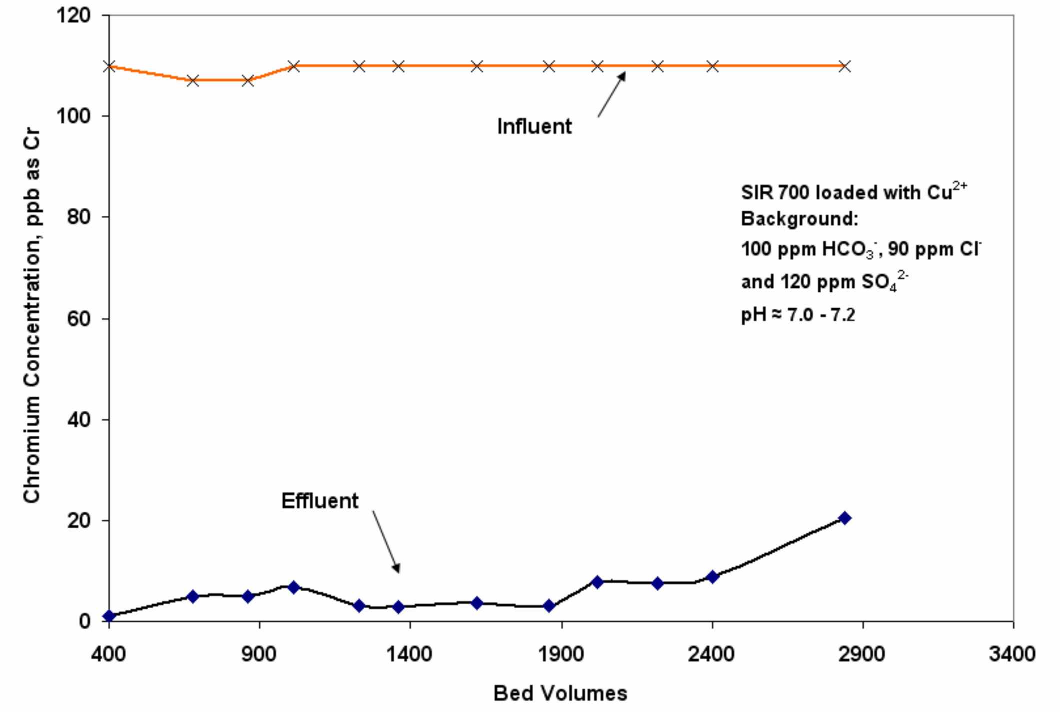

Figure 4. Breakthrough chromate profile with copper-preloaded SIR-700.

EXPERIMENT IV

Figure 5 represents chromate breakthrough profile for Duolite A-7 column run using Glendale well water. Note that the column run continued for more than 25,000 bed volumes. Analysis of the effluent obtained during the run confirmed the presence of only chromium(VI) in the effluent; no chromium(III) was observed in the effluent.

Chromium concentration in the influent was spiked to 200 ppb at 26,000 bed volume. As a result, there was an immediate increase in the concentration of chromate breakthrough. A one-day stop in the column run caused an immediate drop in the effluent chromium concentration (as observed in the curve in the inset of Figure 5). A sharper breakthrough profile was observed after the column run is resumed. This behavior is characteristic of a process rate-limited by intra-particle diffusion. The influent pH during the run was maintained at 5.5. The effluent pH was observed to be around 6.7 during the column run. For nearly every column run, the effluent pH was equal or greater than the influent pH.

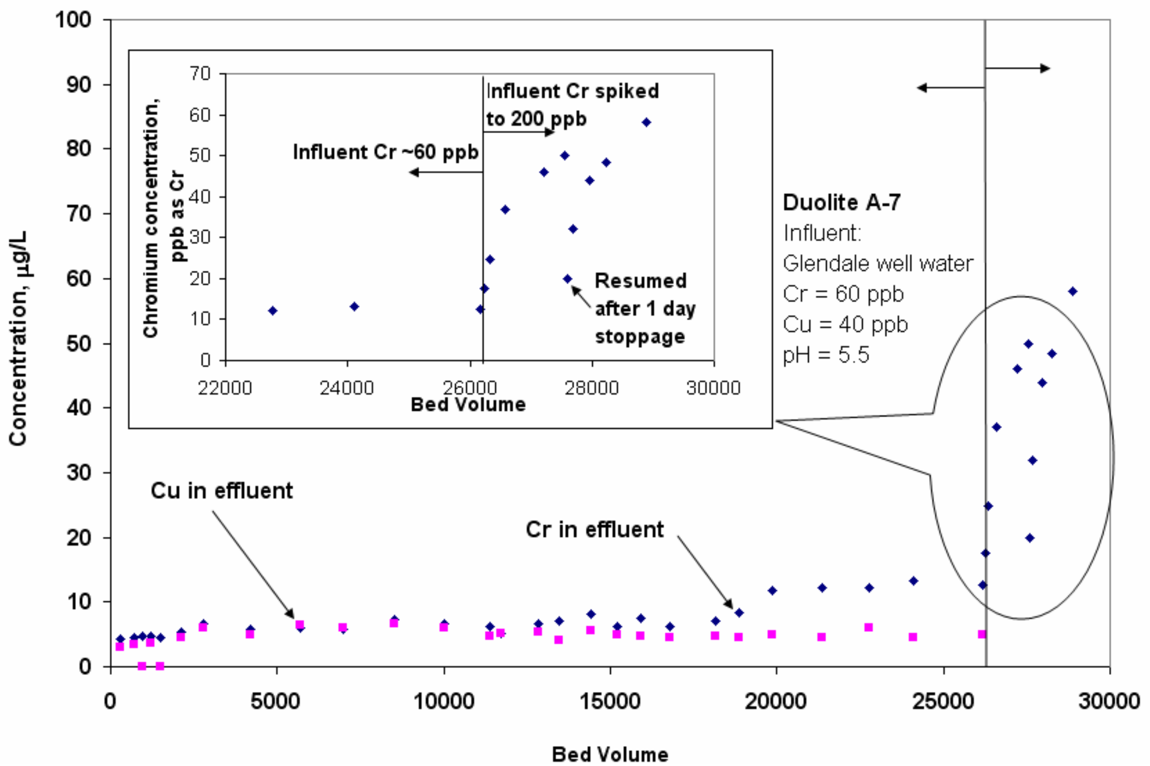

Figure 5. Effluent history of Duolite A7 column run for Glendale well water.

EXPERIMENT V

Table 1 shows results of desorption/elution experiments for exhausted Duolite A-7 and SIR-700 obtained after the field studies at Glendale. Note that Cr(VI) is absent in the eluted solution; Cr(III) is the only chromium present within Duolite A-7 and SIR-700 regradless of the chemical composition of the regenrant.

Table 1

Elution with 6% NaCl & 2% NaOH followed by 2% H_2SO_4

Resin	6% NaCl & 2% NaOH			2% H_2SO_4		
	Total Cr	Cr(VI)	Total Cu	Total Cr	Cr(VI)	Total Cu
	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g
Duolite A-7	0.605	0.006	0.664	2.9	0.00	21.8
SIR-700	0.607	0.012	0.21	0.931	0.00	7.13

EXPERIMENT VI

Figure 6 represents chromate breakthrough profile for SIR-700 with synthetic feed water for which the influent pH was deliberately changed during the column run. For the initial period of the column run, pH of the influent was kept around 7.0. An early breakthrough of 60 ppb was observed after 3800 bed volumes. At that point, the influent pH was reduced to 5.0. Chromate at the exit of the column dropped to 20 ppb.

Figure 7 represents the effect of empty bed contact time or surface loading rate for the removal process inside the column. It is noted that when the surface loading rate is doubled by doubling the flow rate, there was a decrease in the chromium removal performance i.e., chromate at the exit of the column increased. The breakthrough profile, however, returned close to its earlier value when the original flow rate was restored.

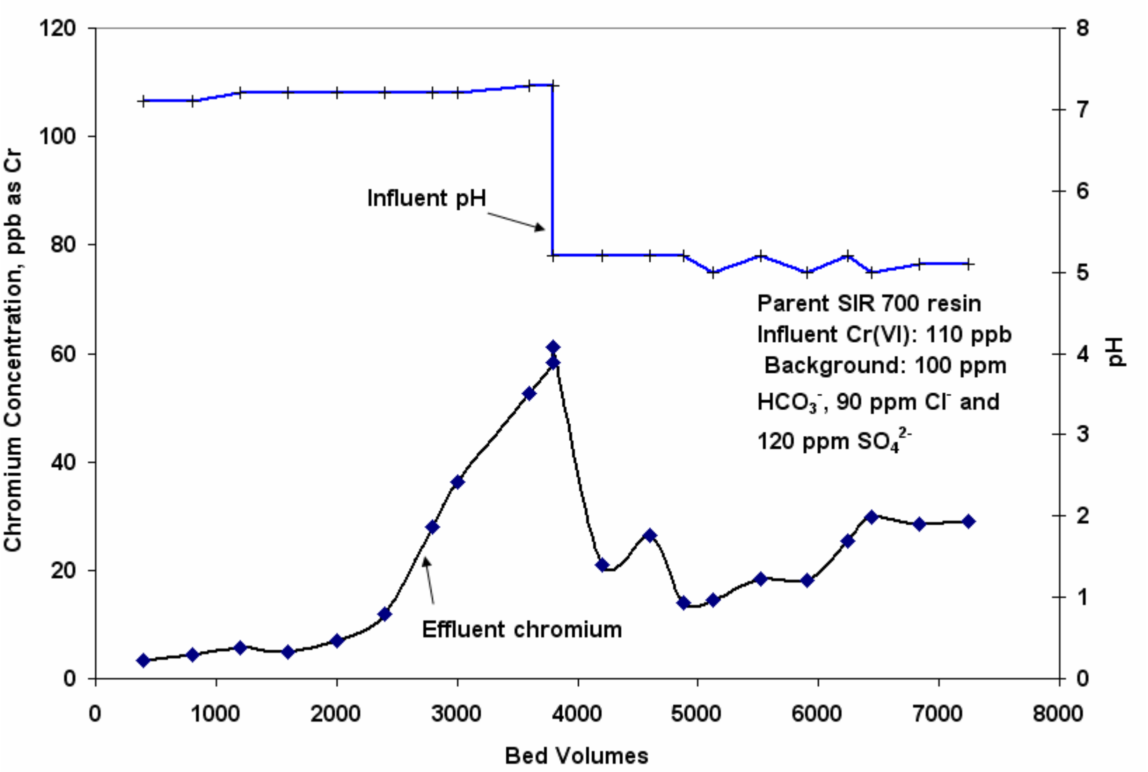

Figure 6. Effect of step change in influent pH on Chromium(VI) removal by SIR-700 during a column run

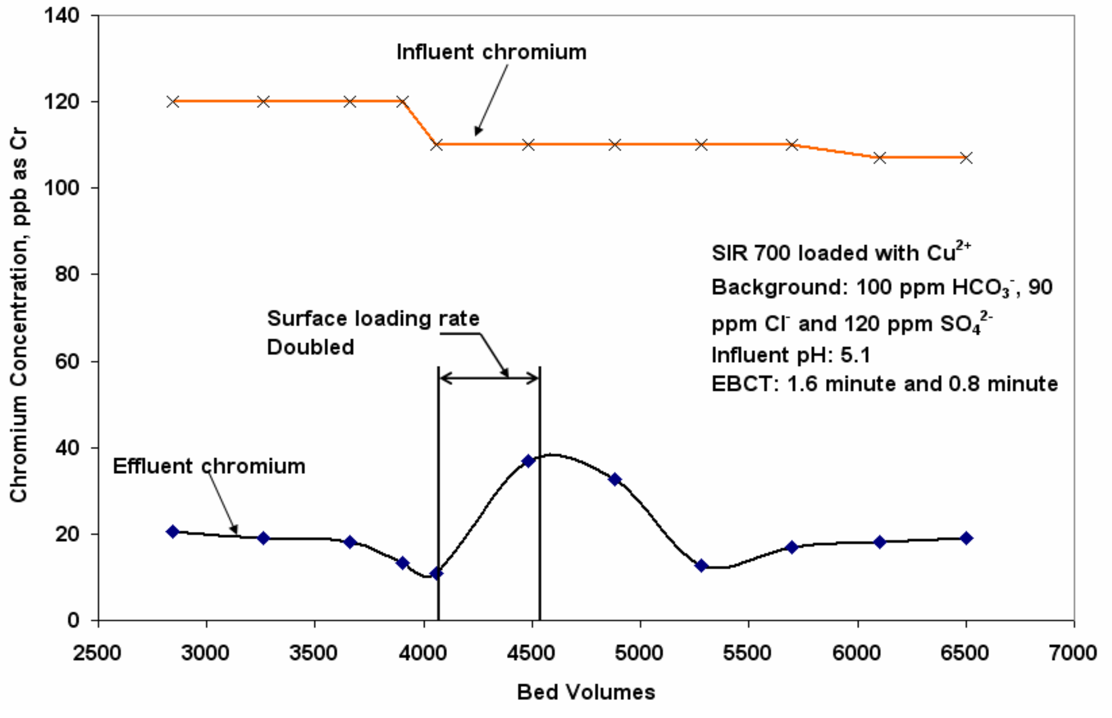

Figure 7. Effect of surface loading rate or EBCT on chromium breakthrough concentration. EBCT was decreased from 1.6 minute to 0.8 minute during the period marked in the figure.