



# Nucleated Precipitation for Heavy Metal Removal and Resource Recovery(1)

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A novel but simple and one-step method for heavy metal removal from industrial plating wastewater has been developed in this study. The new technology is based on using a fluid sand bed to induce nucleated precipitation of heavy metals on the sand surface, as shown in Fig.1.

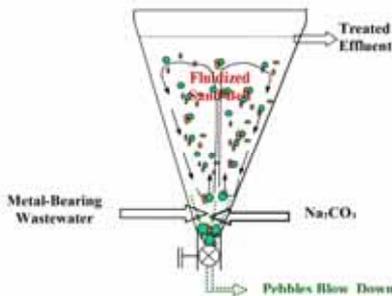


Fig.1 A Fluidized Bed for Metal Stripping through Nucleated Precipitation

In operation, the metal-bearing wastewater is pumped through a fluidized sand column with a simultaneous injection of carbonate solution to raise pH metal precipitation to occur and then deposit on the sand surface (nucleated precipitation) rather than to form discrete metal original sand grains are 0.2-0.3mm in diameter, but quickly grow to a much larger size (up to 2 or 3mm) upon continuous coating of metal precipitates. The larger coated sand particles sink to the bed bottom from which they can be easily removed. New sand can then be added from the top of the stripper. Since the coated particle contains a high level of metal mineral, they can be collected for mineral recovery.

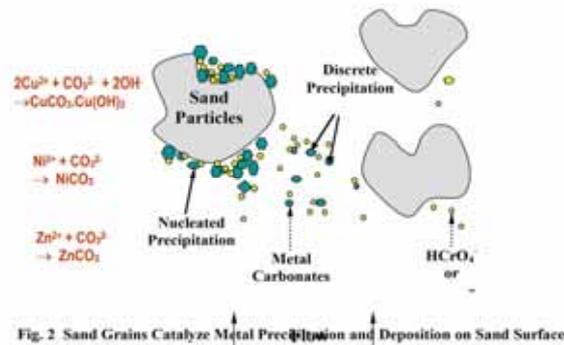


Fig. 2 Sand Grains Catalyze Metal Precipitation and Deposition on Sand Surface

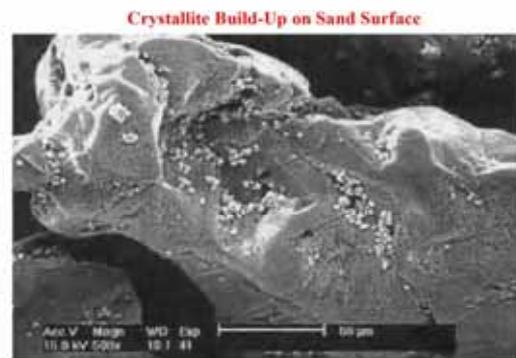


Fig. 3 Electron-micrograph Showing Metal Deposition on Sand Grains



Fig. 4 Applying New Technology in Treating Actual Planting Wastewater in Hong Kong

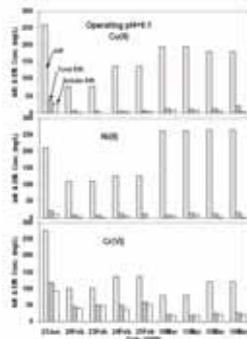


Fig.5 Metal Removal Efficiencies in Treating Actual Planting Wastewater

When the new technology was applied to treating actual planting wastewater in Hong Kong (Fig.4) containing copper, nickel and hexavalent chromium, it was found that at a operating pH of 9.1 the removal efficiencies for both copper and nickel were 95% or higher (Fig.5). At the same time it was surprisingly observed that hexavalent chromium  $Cr^{+6}$ , existing as either  $HCO_3^-$  or  $CO_3^{2-}$  was also removed by 65 to 75% (Fig.5)

Thus, a subsequent study was carried out to identify the mechanisms for the co-removal of hexavalent chromium. It has been identified that two mechanisms are involved: 20% of the co-removal is due to co-precipitation with copper in forming  $CuCrO_4$  precipitates, and 80% through adsorption of bichromate ( $HCrO_4^-$ ) and chromate ( $CrO_4^{2-}$ ) ions onto the copper carbonate precipitates [ $CuCO_3 \cdot Cu(OH)_2$ ]. The two mechanisms are illustrated in Fig. 6.

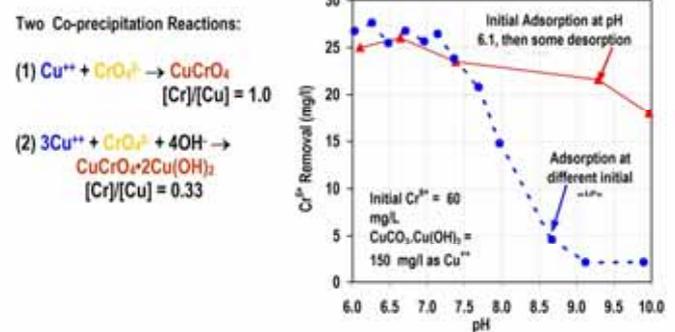


Fig. 6 Co-precipitation and Adsorption of  $Cr^{+6}$  During Copper Precipitation

The reason for the adsorption to take place is due to electrostatic attraction since at pH below 7.5, the copper carbonate precipitates carry positive charges as illustrated by the zeta potential plot in Fig. 7. For this reason the maximum adsorption occurs at pH 6.2-7.0. for mineral recovery.

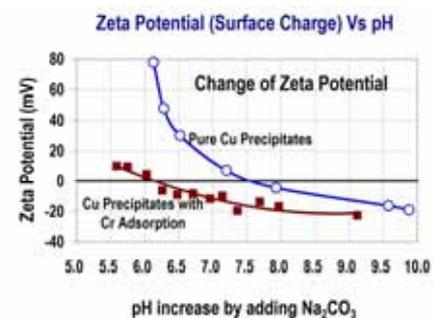


Fig. 7 Changes of Zeta Potential with pH on Copper Carbonate Precipitates

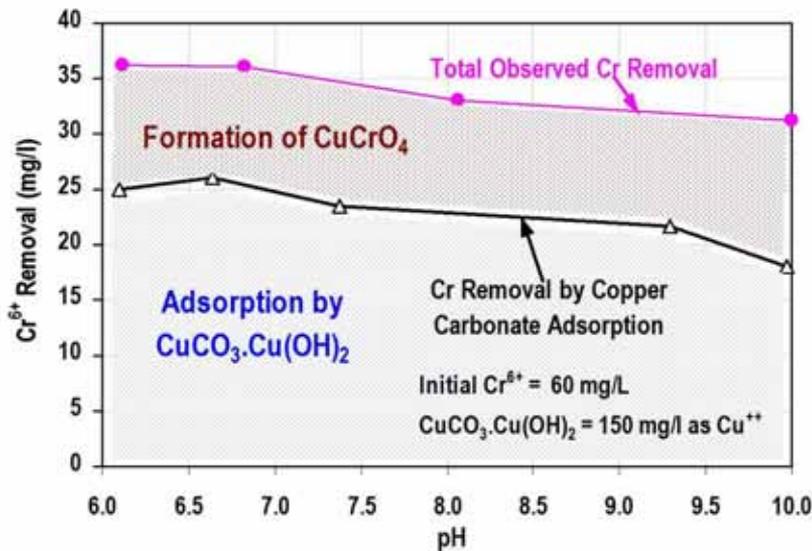


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The relative contributions between co-precipitation and adsorption toward the hexavalent chromium removal is illustrated in Fig. 8. In general, 25% of the co-removal is attributed to co-precipitation (forming  $\text{CuCrO}_4$ ) and the remaining 75% by adsorption.



## Conclusion

1. Nucleation precipitation is a simple cost effective method to strip off heavy metals in a fluidized sand bed.
2. In treating actual plating wastewater at an operating pH of 9.1, the removal efficiencies of copper and nickel are higher than 95%; at the same time, about 65-75% of Hexavalent chromium is also co-removed.
3. Two mechanisms are found to contribute to the hexavalent chromium co-removal: co-precipitation leading to the formation of insoluble  $\text{CuCrO}_4$ , and adsorption of chromate ions on the positively charged copper carbonate precipitates.
4. The main drawback of this new technology is that it normally does not reduce the effluent metal concentration to less than 1.0 mg/L. As such, the treated effluent may need further polishing by ion exchange operation in order to make it comply with the effluent standards.

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