Hazardous Waste Minimization at a Brass Wire Mill

By M.J. Pardus and R.W. Regan

To eliminate hazardous hexavalent chromium from a brass wire-mill waste, hydrogen peroxide was examined in place of chromic acid for pickling, first in bench-scale tests and then in plant tests. Although the elimination of chromic acid requires more rigid control of the wastewater treatment operation and increases the zinc content of the waste-treatment effluent, the economic benefit of substituting peroxide outweighs these disadvantages. Neutralization with caustic soda and membrane ultrafiltration results in an effluent with acceptable concentrations of copper, zinc, lead and nickel.

Many industries are faced with the need to improve their waste management procedures, specifically when hazardous and toxic wastes are involved.’ The ultimate solution is the development and application of a comprehensive management strategy that complies with environmental regulatory requirements, maintains product quality and reduces overall cost. The achievement of this ideal at a brass wire operation of an integrated brass and bronze mill* is the subject of this paper. Stabilized hydrogen peroxide was used in place of chromic acid solution as the oxidizing pickle.

The standard production process for metal forming at the wire mill involved heat treatment, chemical removal of surface oxides and a drawing step. During heat treatment cuprous oxide formed on the wire surface. Removal of the oxide required oxidation to the cupric state. Historically, chromic acid was used for this step, The relatively short working life of the chromic acid pickling solutions and an inability to rejuvenate them imposed an economic penalty. Concern over control of hexavalent chromium during wastewater treatment resulted in a policy to substitute a stabilized hydrogen peroxide/sulfuric acid solution. The impact of the proposed substitution on the wastewater treatment system was not known.

To investigate the effect of the proposed change on the removal of heavy metals, primarily copper and zinc, from wire-mill wastewaters, bench and full-scale testing was undertaken.[2] Observed trends under a variety of test conditions were used to predict any difficulties in meeting federal waste discharge requirements. The impact of co-precipitation of these metals with residual chromium and its effect on the full-scale treatment of process wastewater were examined. Effects on the volumes of generated process wastewater and associated cost factors also were considered.

Background

Wastewater associated with brass wire production has been regulated as a part of the Copper Forming Point Source Category (40 CFR 468). The unit operations of the manufacturing process under study were annealing followed by a water quench, acid pickling and rinsing. Based on the mass of product passing through these operations, mass-based discharge limits[3] (Table 1) were calculated for Cu, Zn, Pb, Cr and Ni discharged from an existing source to a publicly owned treatment works (POTW).

Prior to the installation of a treatment system at the wire mill, concentrated pickle solutions (18,000 to 37,000 L/week) were shipped off-site to a centralized waste treatment facility at a cost of $21,000 to $22,000. Wire-mill spray-rinse wastewaters were bled into the central treatment plant where they were diluted with less concentrated wastes and pretreated prior to discharge to the POTW. Table 2 shows the amounts of copper, zinc and other metals in these rinsewaters. Periodically, the effluent limits were difficult to achieve.

---

*Cerro Metal Products, Bellefonte, PA.

Table 1
Mass-Based Effluent Limits for the Brass Wire Mill

Operation	Discharge limit kg/day* Cr	Cu	Pb	Ni	Zn
Anneal/water quench	0.014	0.09	0.01	0.11	0.05
Pickle bath**	<0.005	0.01	<0.005	0.014	0.005
Pickle rinse	0.032	0.18	0.02	0.23	0.11
Total	0.045	0.272	0.032	0.350	0.163

“Calculated from the pretreatment standards for existing sources (PSES).[3]

**Batch discharge for control of dissolved metals.

Table 2
Representative Metal Discharge from Wire-Miil Rinsewater*

Metal	Discharge, kg/day Min.	Max.	Avg.
Cr	0.09	0.33	0.18
Cu	0.10	0.83	0.45
Pb	0.014	0.10	0.04
Ni	0.014	0.05	0.03
Zn	3.64	8.16	4.94

“Baaed on data collected between June and September, 1984; pH was 6.5 to 7.5.

At the time, a 7 to 10 percent, by volume, solution of sulfuric acid containing 15 to 22 g/L of sodium bichromate was used as the oxidizing pickle. This chromic acid "bright dip" solution had a short working life; no method was known to regenerate the trivalent chromium compounds and the process posed a high cost for treating the hexavalent chromium remaining in the spent acid and rinsewater. Furthermore, a hard chromate film formed on the wire and reduced die life.'

Stabilized hydrogen peroxide was found to be an acceptable alternative for the removal of cuprous oxide from wire surfaces. Peroxide pickling was advantageous because the solution was regenerable, copper could be recovered as copper sulfate by recrystallization or as copper by electrowinning. No residual film was left on the work surface and less costly waste management techniques were possible.[4] A commercially available product** containing 35 percent stabilized peroxide was purchased as a direct replacement for the chromic acid. The pickling tanks contained 1 to 2 percent, by volume, of hydrogen peroxide and 7 to 10 volume percent sulfuric acid. Peroxide pickling generated only 3800 to 7600 L/week of spent acid waste.

Equipment Selection

A space limitation was a major factor in equipment selections After a review of available technologies, membrane filtration was selected for a field trial. Neutralization of the waste with liquid caustic soda followed by membrane filtration produced a high quality effluent (Table 3). The use of liquid caustic soda avoided the formation of excess solids associated with lime neutralization of acid-bearing waste. Neutralization, which precipitated heavy metals, followed by membrane filtration was ultimately selected as the preferred treatment process based on the results of pilot plant studies. Elimination of chromic acid from the wire mill could not proceed until the full-scale system started up. Pending such a start-up, a series of bench scale treatability studies was conducted to evaluate the impact of the proposed in-plant process changes on the removal of heavy metals from the wastewater.

The waste treatment system*** consisted of skid-mounted assemblies for precipitation of hydroxides, membrane filtration, sludge dewatering and membrane cleaning (Fig. 1). The system was fully operational within

Table 3
Results of Pilot Testing Using Caustic Neutralization and Membrane Filtration

Metal	Concentration, mg/L Influent*	Effluent
Cr	270	<0.1
Cu	100	<0.1
Pb	4	<0.1
Ni	2	<0.1
Zn	235	<0.1

*Influent sample for the treatability study was composited from rinsewater and spent acid.

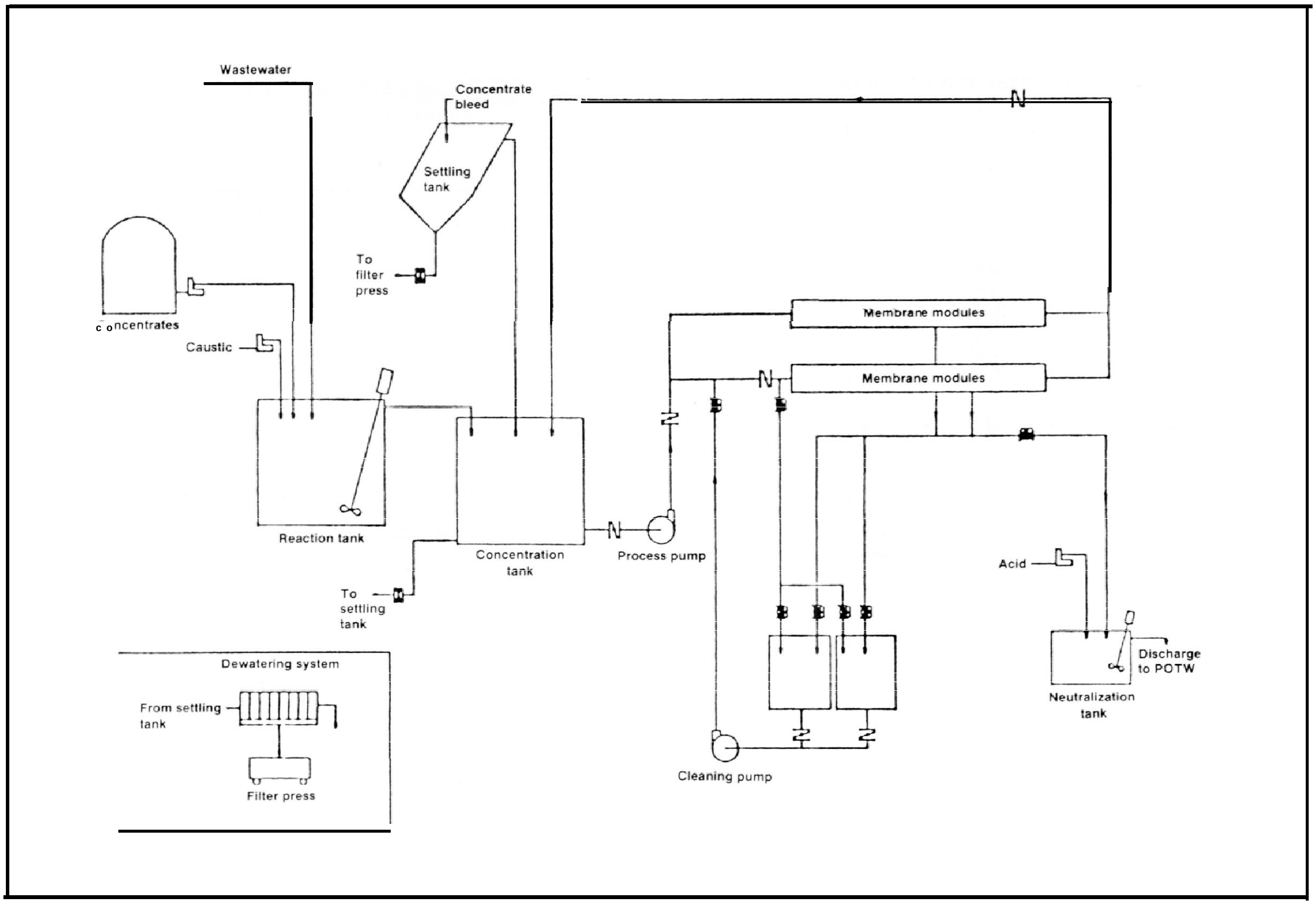


Fig. 1—Process diagram for brass wire milf waste treatment.

**CO-BRA-SOL, stabilized hydrogen peroxide (35 percent), Electrochemical Division of Dart Industries, Youngstown, OH.

***Model UF2610, Memtek, Billerica, MA.

two weeks of delivery. The collected rinsewaters were pumped to the reaction tank and neutralized with 50 percent caustic solution. Spent acid was bled directly into the reaction tank. The neutralized wastewater flowed by gravity to the concentration tank and circulated through the membranes at a pressure of 2.8 kg/cm^2 (40 lb/in.^{2}).

The membrane filtration system was operated in a cross-flow mode using 25-mm diameter tube geometry. In cross-flow filtration, fluid flow is parallel to the filter media (Fig. 2). Solids are separated at only one surface layer or plane. In conventional barrier filtration, separation occurs at several layers of filter media. The tubular geometry was preferred due to its resistance to fouling}

Fluorocarbon-based membranes were set up in two parallel trains, each with six modules in series. Each module consisted often tubular membranes providing 1.4 m^2 of surface. The neutralized wastewater was pumped through the membranes at a high velocity (4.6 to 6.0 m/sec), which resulted in a turbulent flow regime. The rejected solids were fluidized and scoured under these flow conditions, keeping the membranes clean while maintaining acceptable flux rates. With this membrane system, flux rates of 800 to 1600 L/day/m^2 of membrane were achieved at a pressure of 2.8 kg/cm^2 (40 lb/in.^{2}).

The permeate was collected and the pi-f was adjusted as necessary, prior to discharge to the POTW. The rejected solids were concentrated and returned to the concentration tank where they were bled-off to the sludge dewatering system. A plate and frame filter press was used to dewater the residual solids.

The treatment system, designed to produce a minimum of 90 L/min, was brought on line in May, 1986. Capacity was expandable to maintain a maximum flow of 166 L/rein by the addition of a second membrane module rack. Cleaning the membranes every two weeks with dilute hydrochloric acid has maintained permeate rates of 375 to 450 L/min without adding additional membranes, The required cleaning time was 30 to 45 min.

Bench Scale Test Methods

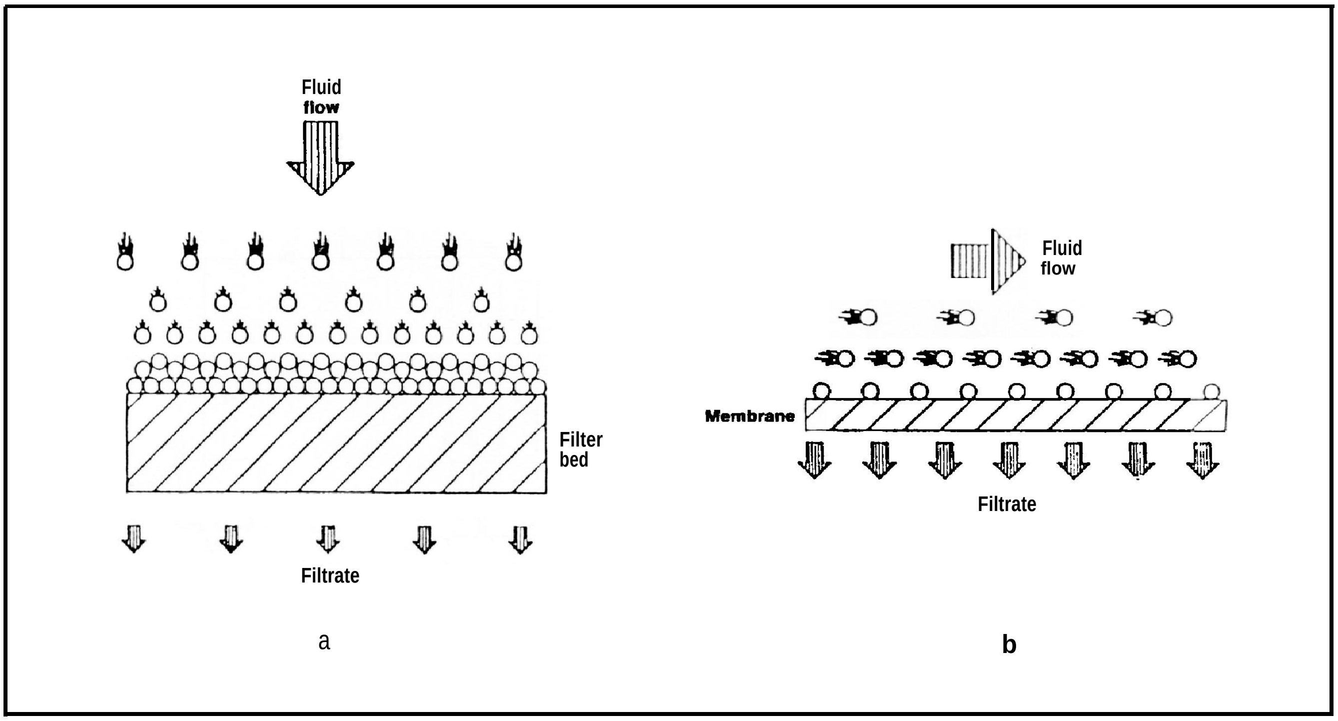
To determine metal removal as a function of pH, neutralization tests were conducted by titrating a 25-mL aliquot of process or synthetic waste with 1.0 N sodium hydroxide to a given pH. The neutralized sample was immediately filtered through a 0.45 µm Whatman membrane filter using conventional vacuum filtration and the filtrate was acidified with 2 mL of 50 volume-percent nitric acid. Flame atomic adsorption spectroscopy with an air-acetylene flame was used to determine metal concentrations.

Reagent-grade copper sulfate, zinc oxide and sodium bichromate were used to prepare some synthetic waste solutions. Each compound was dissolved in deionized water containing 5 volume percent of reagent-grade sulfuric acid, to produce a final concentration of 300 to 400 g/L of each metal.

Table 4
Composition of Bench-Test Solutions

	Concentration, mg/L					
	Reduced chromate	Synthetic wastes				Peroxide
Metal	waste	1	2	3	4	waste
Cu	414	329	*	382	350	648
Zn	423	*	378	419	383	663
Cr^{3+}	688	*	*	*	336†	11
Pb	1.4	*	*	*	*	0.8
Ni	5	*	*	*	*	2
Fe	4	*	*	*	*	7
pH	2.6	1.3	1.3	1.3	1.3	1.86

*None added
†Hexavalent chromium



a

b

Fig. 2—Comparison of (a) barrier and (b) cross-flow membrane filtration.

Table 5
Bench Test Results

	Reduced Chromate Waste			Synthetic/Peroxide Waste		
Metal	Initial pH[a]	pH range[b]	Conc., mg/L[c]	Initial pH[a]	pH range[b]	Conc., mg/L[c]
Cu	4.1	7.3-11.8	0.01	5.4	8.0-11.3	0.03
Zn	4.3	7.5-12.0	0.05	7.0	9.2-10.4	0.07
Pb	3.9	6.0-12.0	0.04	4.4	6.5-11.0	0.04
Ni	4.0	7.0-12.0	0.04	6.7	8.0-12.0	0.02
Fe	4.0	5.0-13.0	0.07	3.8	6.0-12.5	0.06

---

[a] pH when significant precipitation occurred.
[b] pH range of optimum metal removal
[c] Average concentration over optimum pH range

Process waste samples were obtained from the spent acid collection pit, representing a 3 to 5-day accumulation of the acidic waste. Two parts of each sample were diluted with 15 parts of distilled water to approximate the spent acid feed rate for the waste treatment system.

Full-Scale Tests

Full-scale tests were conducted under process conditions at the brass wire mill. Data were generated by varying the neutralization set point to achieve the desired pH. A 24-hr, flow-proportioned composite sample was obtained by a solenoid-driven diaphragm pump from the permeate collection tank. Influent samples were composite from grab samples taken every 4 to 8 hr. The composite samples were acidified with 1.5 mL/L of nitric acid and metal concentrations were determined by flame adsorption spectroscopy.

Bench Scale Results

The compositions of the process solutions used for bench-scale tests are given in Table 4. Table 5 shows the residual metal concentrations after neutralization. Based on these studies, it appeared that Cr^{3+} ions broadened the pH range for the effective removal of heavy metal ions. Although the proposed substitution of hydrogen peroxide for chromic acid was expected to have a severe, adverse effect on the control of the final zinc concentration, the results indicate that copper and zinc removal was only slightly enhanced by the presence of Cr^{3+}; Pb, Ni and Fe concentrations were marginally affected. The experimental Pb and Ni concentrations were several orders of magnitude lower than those predicted from thermodynamic calculations,[2] but the Fe concentration was several orders of magnitude higher.

A previous study indicated that some threshold level of Cr^{3+} may have to be present for enhanced metal removal.' An additional study is needed to establish this level.

Full-Scale Results

The influent metal concentrations during full-scale tests are shown in Table 6. Concentrations and mass-discharge levels for t rested wastewaters are given in Tables 7 and 8, respectively.' The data for the peroxide wastewater treatment were generated during the six-month period from

Table 6
Metal Concentrations of Influent During Full-Scale Tests

	Concentration, mg/L					
	Chromate wastewater			Peroxide wastewater		
Metal	Min.	Max.	Avg.	Min.	Max.	Avg.
Cr	152	1447	500	0.3	10.0	4.5
Cu	16	846	370	5	1551	320
Pb	1.0	25.0	7.5	1.1	3.6	2.4
Ni	0.8	11.0	3.9	<0.1	3.8	1.1
Zn	88	938	430	31	1154	270

Table 7
Metal Concentrations of Effluent During Full-Scale Tests

	Concentration, mg/L					
	Chromate wastewater			Peroxide wastewater		
Metal	Min.	Max.	Avg.	Min.	Max.	Avg.
Cr	0.03	0.51	0.24	0.01	0.28	0.07
Cu	0.03	0.09	0.05	0.02	0.44	0.06
Pb	0.01	0.06	0.03	0.01	0.39	0.06
Ni	0.01	0.12	0.03	0.01	0.15	0.04
Zn	0.03	0.14	0.10	0.09	3.38	0.29

Table 8
Mass-Based Metals Discharge During Full-Scale Test

	Discharge, g/day					
	Chromate wastewater			Peroxide wastewater		
Metal	Min.	Max.	Avg.	Min.	Max.	Avg.
Cr	0.9	44.5	16.8	1.4	9.5	4.5
Cu	2.3	6.4	3.6	1.4	18.6	4.0
Pb	0.9	5.0	2.3	1.4	15.0	4.0
Ni	1.4	8.2	2.3	1.4	7.8	3.2
Zn	2.3	17.3	6.8	5.0	240.6	22.2

Table 9
Annual Brass Wire Mill Treatment Costs

Operation	Before pretreatment	Pretreatment + chromates	Pretreatment + peroxide
Off-site treatment	$41,000	$13,800	–
On-site treatment	—	$ 9,600	$ 13,600
Sludge disposal	$24,000	$14,200	$ 8,500
Process chemicals	$36,200	$32,700	$35,900
Total	$101,000	$70,300	$ 58,000

May to October, 1987. The results agreed with the outcome of the bench-scale studies. Cr^{3+} lowered metal concentrations in the treated wastewater and increased treatment system stability. Peroxide treatment required strict control of pH during neutralization and the spent acid-feed rate. Metal removal efficiency was measurably reduced by the elimination of chromic acid from plant processes. The change from chromic acid to hydrogen peroxide had a greater effect on the removal of zinc than on copper. Therefore, control of zinc was the limiting factor,

Economic Evaluation

Process economics were evaluated in three phases: (1) before implementation of the pretreatment plan, (2) after the treatment was installed but before chromic acid use was phased out and (3) after hydrogen peroxide was substituted for chromic acid. The major economic factors considered included the cost of on-site and off-site treatment, sludge disposal cost and the cost of process chemicals and water. Cost data generated in 1987 are summarized in Table 9. Reference 5 provides a more complete description of process modifications and economics. Overall waste treatment costs were reduced $43,200/yr.

Conclusions

Treatment of wire-mill wastewaters by using caustic neutralization and ultrafiltration exhibited a metal removal efficiency of over 99 percent for Cr^{3+}, Cu and Zn and a removal efficiency above 90 percent for Ni and Pb. Effluent metal concentrations averaged less than 0.1 mg/L except for Zn which averaged less than 0.3 mg/L. Cr^{3+} has a beneficial effect on the removal of these metals by hydroxide precipitation, but this benefit was outweighed by the potential environmental liabilities associated with Cr^{6+} in the wastewater.

Substitution of stabilized hydrogen peroxide in sulfuric acid for chromic acid required more stringent control over waste treatment operations. Overall, cost-effective compliance with federal environmental regulations was achieved. An audit of existing plant processes and implementation technology alternatives has resulted in significant improvements in waste treatment efficiency and hazardous waste minimization and has reduced waste treatment costs. Use of the peroxide pickling solution has maintained product quality in the wire mill.

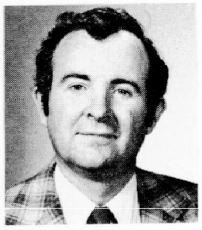
Acknowledgment

The support of the management of Cerro Metal Products is acknowledged. A description of the research was presented at the Purdue University Industrial Waste Conference, May 1988.

References

1. R.W. Regan and C.E. Draper, *Plat. & Surf. Fin.,* 74, 58 (Aug. 1987).
2. M.J. Pardus, Material Substitution: A Study of the Effect of Waste Minimization on Effluent Metal Concentration, Unpublished MS thesis in Environmental Pollution Control, 65 pp. (Aug. 1987).
3. Development Document for Effluent Limitations, Guidelines and Standards for the Copper Forming Point Source Category, U.S. EPA, Washington, DC (Oct. 1982).
4. M.L. Elias, *Metal Progress,* (Jun. 1981).
5. M.L. Pardus, Cost Effective Compliance with the Pretreatment Standards: A Case Study in Waste Minimization, Proc. 9th AESF/EPA Conference on Pollution Control for the Metal Finishing Industry, U.S. EPA, Washington, DC (Oct. 1982).
6. T.V. Tran, Chem. Eng. *Progress,* 81 [3],29 (1985).


Pardus


Regan

About the Authors

Michael J. Pardus was the chief chemist for Cerro Metal Co., Bellefonte, PA, until May, 1988. He is now affiliated with Hart Environmental Associates, Penn Center, Bldg. 3, Suite 106, Pittsburgh, PA 15276-0103. Mr. Pardus received a MS in environmental pollution control from The Pennsylvania State University in August 1987. The subject matter of this paper is based on his graduate thesis.

Dr. Ray W. Regan is an associate professor of civil engineering and the director of the Office of Hazardous and Toxic Waste Management, Environmental Resources Research Institute, Land and Water Research Building, Penn State University, University Park, PA 16802. Dr. Regan received a PhD in environmental health engineering from Kansas University.