A MODIFICATION OF COLUMN-TYPE HUMIDITY CELLS TO ACCOMMODATE VERY FINE-GRAINED MINERAL PROCESSING WASTES[1]

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Abstract. Despite numerous shortcomings, kinetic testing incorporating a variety of humidity cell configurations remains an important component of mining waste characterization. The ASTM D 5744-98 and similar devices offer advantages for controlling experimental variables and increasing reproducibility. However, the design is limited in its ability to accommodate very fine-grained process wastes such as autoclave residues due to low permeabilities that restrict fluid movement and may impose diffusion-rate limitations on the oxidation processes. A method has been devised to impregnate fine-grained wastes in a highly permeable fiber substrate that appears to allow excellent access of both air and elution water to individual waste particles.

Background

Despite numerous shortcomings and common misuse, laboratory-scale kinetic testing incorporating a variety of humidity cell configurations remains an important component of mining waste characterization. A review of apparatus configurations and an update of current practices for humidity cell interpretation are provided by Lapakko (2002). Typical siliceous waste rock, crushed and sized to approximately 1 cm, is perhaps ideal for laboratory kinetic testing, but other mining-related materials are less well suited. Many important process wastes pose significant problems for air and water exposure in kinetic cells due to the comminution involved in their preparation, especially when fine or ultra-fine grinding are necessary for flotation, bio-leaching, or low pressure autoclave oxidation. Particle sizes in these latter cases are commonly less than 10 microns (Lichter and Davey, 2002).

Of those methods discussed in detail by Lapakko, op. cit., only two (ASTM [1996, with revisions in progress] and Morin and Hutt [1997]) address fine-grained mine waste, specifically tailings. Neither addresses ultra-fine wastes. Both methods involve the placement of one kg of tailings in columns (20.3-cm [8-inch] and 16.5-cm [6.5-inch] I.D, respectively) and then allow dry, followed by humidified, air to circulate only over the top surface. Elution in both cases involves the entire mass of tailings, and the latter method requires stirring of the wetted mass.

While these techniques may be seen to emulate actual exposure geometries (e.g., the surface of a tailings deposit), the unknown and possibly un-reproducible mass of tailings actually exposed to O_2 during any given weekly cycle places limitations on the quantitative interpretation of results. After any soluble phases present prior to testing (e.g., gypsum) have been eluted during the early weeks of testing, subsequent weekly eluate concentrations are expected to be a function of the total surface area of each reactive phase of the test material in the same way that intrinsic reaction rates are related to surface area. Consequently, an important part of the success, reproducibility, and even efficacy of laboratory-scale, humidity cell-based kinetic testing is the ability of reactants (i.e., dry and humidified air) to have free access to a known fraction (ideally, 100 percent) of the surfaces of the material placed in the cells.

"Free access" implies, for example, that observed redox reaction rates not be oxygen diffusion-rate limited. In addition, efficient weekly elutions of reaction products require access of water to all surfaces and in sufficient volumes so that dissolution of those products is not solubility limited. These factors are not likely to impose limitations when relatively coarse and structurally stable materials are placed in humidity cells, especially in column configurations. However, for fine-grained process wastes and the methods cited above, free access to oxygen will be limited to a relatively thin zone below the air/waste surface, and oxygen diffusivity will vary strongly with the decreasing moisture content as the sample dries following elution (Tibble and Nicholson, 1997).

Development of an Apparatus Modification

The humidity cell reported here was initially designed to evaluate the oxidation of elemental sulfur in fine-grained process wastes. To allow adequate exposure of ultra-fine particles to air flow and to retain those particles in the humidity cell during repeated weekly elution, it was reasoned that particles would need to be dispersed in a porous medium that could permanently adhere the particles. Initial attempts to disperse the material among pumice grains and to impregnate filter paper and soxhlet thimbles met with limited success. However, a suggestion to

employ commercial water filters proved highly workable (Wildeman, person. comm.). The type of filter selected is available under multiple brands in retail home improvement stores and consists of cotton yarn spiral-wound onto a perforated plastic mandrel. The cylindrical filters measure approximately 5 cm (2 inches) in diameter by 25 cm (10 inches) in length (nominal), and the thickness of the cotton yarn filter media itself is approximately 1.25 cm (0.5 inches). After impregnation with the subject waste material, the filter was placed inside acrylic cylinders normally used for humidity cell testing following ASTM D 5744-98 procedures, and the cells were operated in a similar manner. Figure 1 illustrates the final assembly and provides operational details.

Impregnation of the tarred filter cylinder was accomplished by first preparing a dilute (low solids content) slurry of the autoclave solids in the process liquor. Due to the presence of soluble gypsum in the residue and the desire to maintain gypsum saturation, the liquor was not diluted with water. The slurry was then forced to circulate through the filter media via a peristaltic pump. Circulation continued with periodic replenishment of the solids content until a sufficient mass of solids was visually determined to have been retained by the filter. After impregnation, the filter was allowed to air dry to a stable weight and the amount of retained residue determined by difference. For six filters impregnated with various ultra-fine-grained materials, retained residue masses ranged from 15 to 25 g. The small mass of sample was a concern but considered acceptable when calculations indicated that oxidation of less than one percent of the sulfur would be detectable by determination of sulfate in the weekly eluates. No tests were conducted to determine if significantly larger sample masses could be impregnated in the filter media.

After drying, the filter was prepared for experimentation by closing the bottom of the central filter cylinder with a stopper and placing the cylinder into the humidity column. The upper end of the central filter cylinder was then connected to an external port through a tight-fitting lid to the column. At the beginning of the seven-day cycle, (dry) laboratory air was introduced into the annular space outside the filter cylinder via the bottom of the column and forced to flow through the filter containing the experimental waste material and exit the column via the port connecting the central cylinder to the outside. After three days, the laboratory air supply was redirected to a humidification tower and then allowed to flow through the column as before. Air flow was terminated after the sixth day. The design necessitated that 100 percent of the introduced air flow through the filter containing all the experimental waste. It was assumed that each particle of waste was thoroughly aerated.

Elution of the waste was accomplished by flooding the humidity cell with a known volume of deionized water sufficient to fully saturate the cotton filter media. Approximately 350 ml was required. A low-volume peristaltic metering pump was then used to circulate the fixed volume of water from the internal cavity of the filter to the annular volume surrounding the exterior of the filter. In this way, fluid movement was always from the outside to the inside of the filter, and any resultant waste particle movement was into deeper portions of the filter. Virtually no suspended matter was observed in the eluates, suggesting insignificant losses of waste material from the cell. Circulation continued until the water volume was completely cycled three times (about 1.5 hours). Following circulation, the humidity cell column was gravity-drained, and the eluate volume was measured, analyzed for pH and electrical conductivity, filtered, and acid-preserved for analysis.
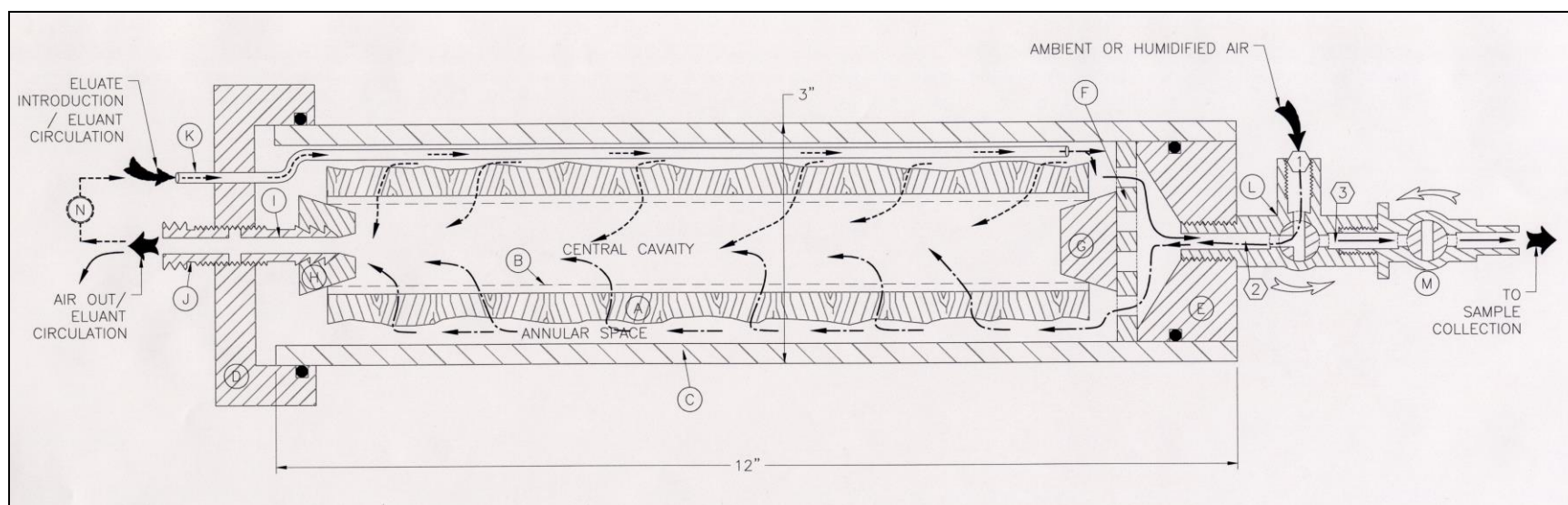
Figure 1. Cross-section of modified humidity cell for investigation of fine and ultra-fine materials. Relative dimensions are not exact in order to facilitate illustration.

Dash-dot flow arrows: Represent path of air (dry and humidified) during the first six days of the seven-day cycle. Dashed flow arrows: Represent the path of circulating eluate water introduced on the seventh day of the seven-day cycle. Solid flow arrows: Represent the path of eluate solution during draining following circulating step.

A. The spiral-wound cotton yarn filter element of a commercial coarse particulate water filter. Thickness of the cotton filter material is approximately 0.45 inches (1.1 cm). Sample residue solids were impregnated into the cotton filter material by circulating a dilute residue slurry through the filter from the outside to the inside using a peristaltic pump. Slurry was prepared by adding small quantities of residue solids to clear supernatant. B. Perforated plastic mandrel on which the filter was wound. Provides support and allows free passage of water through the filter media. C. Body of the humidity cell, cast acrylic, clear, 3-inch O.D., 0.25-inch wall thickness, 12 inches long. D. Cap, Delrin, fitted with Viton O-rings, ported, and tapped to receive fitting (see J. and K.). E. Collection base, Delrin, fitted with Viton O-rings, ported and tapped to receive fitting as shown (see L.). Conical upper surface facilitates drainage to central opening. F. Lower support plenum, Delrin, equipped with multiple 0.25-inch-diameter holes to allow drainage. Can be replaced with 316 stainless steel screen if necessary. G. Lower stopper, neoprene, solid. Designed to seal the bottom end of the central cavity. H. Upper stopper, neoprene, one-hole. Designed to connect the central cavity to the port in the cap through connectors I and J. I. Stopper connector, nylon, one end barbed, one end threaded. J. Cap connector (optional), 316 stainless steel. May be capped during non-operation. K. Eluate in-flow circulation tube, 316 stainless steel. Actual connection through cap is made with a bulkhead connector that can be fitted with a end-cap to prevent air escape during six days of air flow. The tube allows circulating eluate to be introduced into the annular space from which it is drawn through the filter into the central cavity and is withdrawn via a 316 stainless steel tube temporarily inserted through I and J into the central cavity. Circulation is affected by a peristaltic pump (N) (dashed arrows). Path of the eluate is illustrated by the red flow arrows. L. Three-way valve, Delrin. Allows connection 1 and 2 or 2 and 3 only. When 1 and 2 are connected ambient (dry) air or humidified air is allowed to flow into the annular space and can only escape by flowing through the filter and around impregnated residue solids and out through the central opening in the cap (dash-dot arrows). When 2 and 3 are connected (and M closed) the cell is ready for circulation of eluate. Upon opening M, the eluate may be drained (solid arrows). M. Two-way valve, nylon. Remains closed except for draining eluate.

Results for the initial use of the apparatus were favorable, producing consistent curves of decreasing concentrations. After approximately 30 weeks of operation, a solid Delrin plastic cylinder was placed in the central filter cavity to decrease the eluate volume to between 150 and 200 ml and thus increase the constituent concentrations above detection limits.

Figures. 2 through 5 illustrate selected results obtained from two different waste materials. Waste A was confirmed to contain less than 2 wt% gypsum, thus allowing a rapid decrease in eluate sulfate concentrations to less than 100 mg/L. Waste B, on the other hand, contained in excess of 10 wt% gypsum and supported higher eluate sulfate concentrations for longer periods of time. It was possible to closely approximate the early (up to five weeks) observed cumulative sulfate elution curves using a simple mass balance model based on initial gypsum mass, gypsum solubility, residual dissolved solids contained in the initial liquor or the previous week's eluate retained in the filter, and measured eluate volumes. After three to five weeks, sulfate continued to be released in excess of what the model predicted due to gypsum solubility, indicating another source of sulfate – presumably derived from elemental sulfur oxidation.
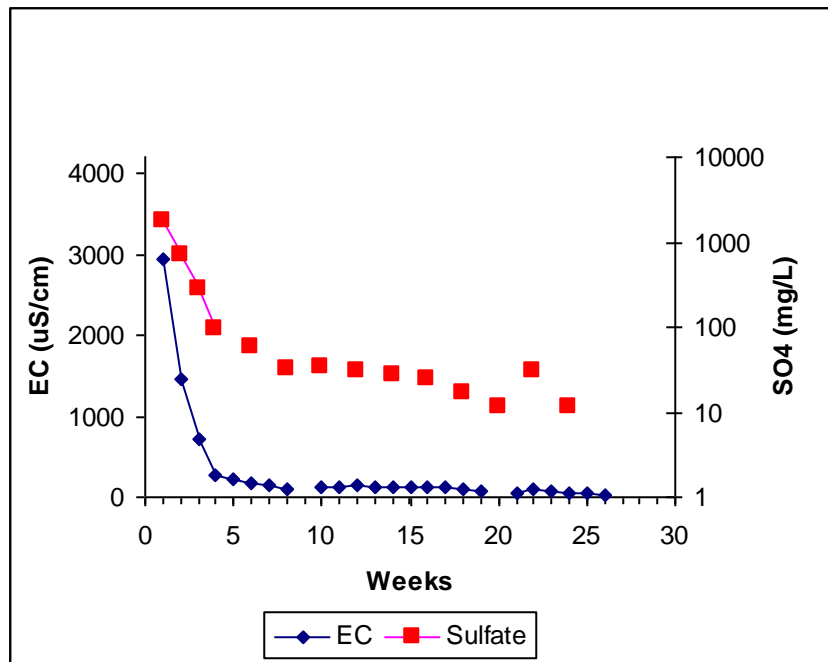

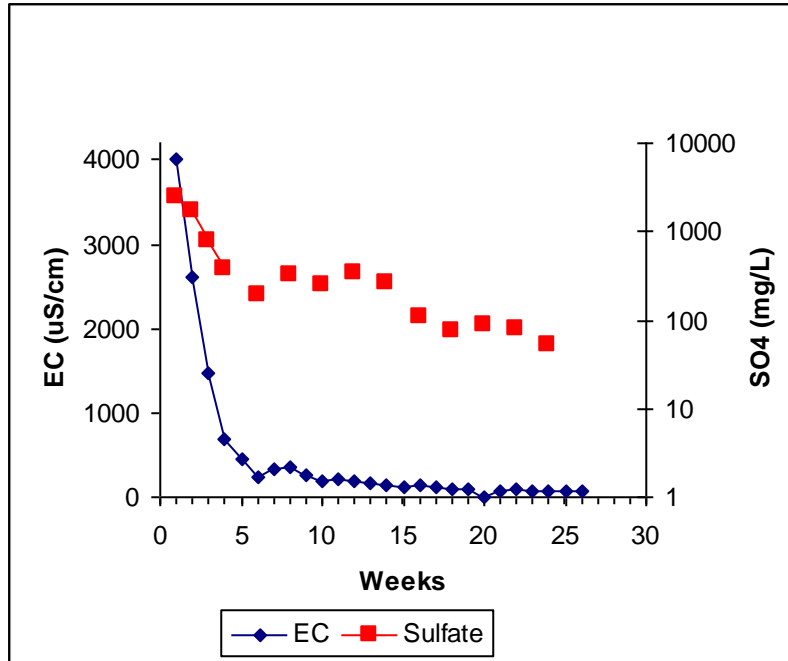Figure 2. Sulfate and electrical conductivity as a function of time for Material A.

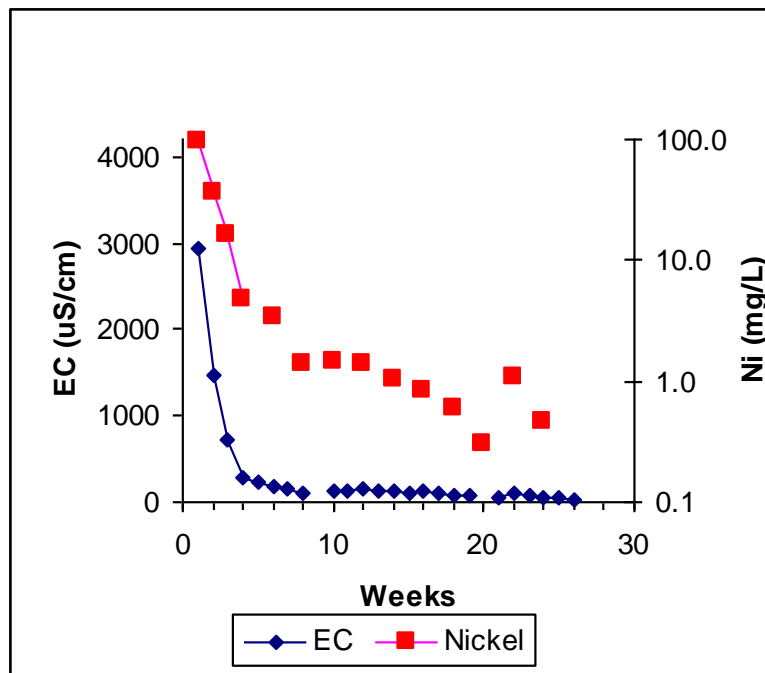Figure 3. Sulfate and electrical conductivity as a function of Time for Material B.

Figure 4. Nickel and electroconductivity as a function of time for Material A.
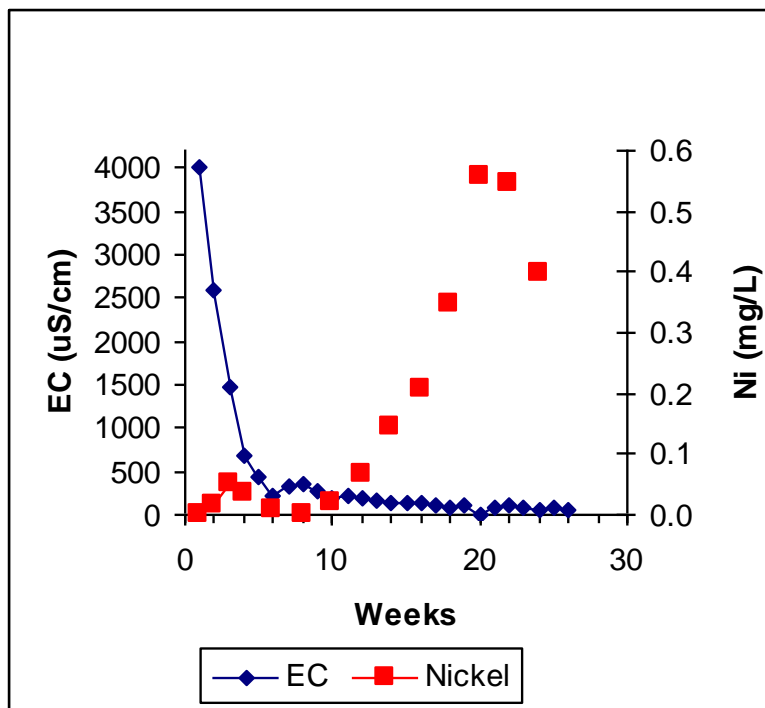
Figure 5. Nickel and electroconductivity as a function of time for Material B.

The reconciliation of the observed eluate concentrations with the model was taken as a first-level indication that the humidity cell was operating as intended. Figures 4 and 5 illustrate the ability of the cell to reveal very different trace element behaviors over the course of nearly 30 weeks of experimentation. Figure 5 in particular confirms that the apparatus is capable of detecting subtle reactions initiated after the initial flushing of soluble sulfates.

At present the apparatus is considered applicable for ultra-fine-grained waste materials but may be adaptable to coarser material such as typical tailings with modification. Disadvantages include small sample size and labor associated with elution. The small sample size clearly implies the need for care in obtaining representative experimental material. However, no upper practical limit for impregnated waste mass is known, and additional peristaltic pumps would reduce elution time and effort. A quantitative demonstration of the uniformity of air and water circulation has not been performed, and such tests may indicate other modifications in design.

Concerns have been raised regarding the chemical stability of cotton yarn in the presence of acid that would be expected from sulfide mineral oxidation. Degradation of the cotton could release particles and potentially compromise eluate analysis. The significance of these concerns is unknown at present.

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