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Mark,

I have reviewed the two OSHA reports, photographs taken and reported in these reports, Powell's web site and several associated references including two patents filed by Powell concerning their electro-coagulation device and other papers pertaining to these devices, particularly where arsenic removal is of importance.

It is my professional opinion based on a reasonable degree of scientific certainty that Powell Water Manufacturing Company failed to meet recognized industry standards in the design, manufacture and operation (particularly on January 21, 2005) of the electrocoagulation unit. Moreover, Powell's employee, Mr. Rasmussen, failed to meet industry standards for industrial safety and hygiene. It is my opinion that these failures clearly caused Mr. Crutch and Mr. Wheeler to be injured on Jan. 21, 2005.

The following report details my opinion in this matter.

Sincerely,

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Description of what occurred on January, 21, 2005

Electro-coagulation is a technology originally developed in 1906 for wastewater treatment that involves the use of an electro-chemical cell to coagulate a wide range of pollutants including dissolved metals allowing the separation by sedimentation or formation of flocs and by filtration. Electro-coagulation provides counter-ions (ions of opposite charge) that neutralize ions in a solution by chemical reaction to form insoluble salts. The process disrupts electrostatic colloidal suspensions and ionic solutions. The counter ion coagulant is produced from an iron electrode that is consumed in the electrocoagulation process. For arsenic, it is desired to form insoluble iron (III) oxyhydroxidearsenic complexes from the hydrolysis of water into H₂ and OH⁻, and O₂. Arsenic is a metalloid so it can bond both as a metal and as a non-metal with the most common oxidation states being -3 such as in arsine (AsH₃) and +3 (areinite) such as in As₂O₃. A less toxic +5 oxidation state (arsinate) is also common such as in As₂O₅. The arsenic oxides are soluble in water and form an acidic solution. Iron can form insoluble oxides with arsenic, FeAsO₄, or sorption of As can occur to insoluble iron oxides, hydroxides and amorphous iron. (Iron(III) oxyhydroxide-arsenic complexes are noted as the most common natural mechanism of arsenic removal from the environment [Cullen & Reimer 1989].) Hydrolysis of water is a necessary reaction for the production of iron, iron oxides and iron hydroxides in the electro-coagulation unit. This process produces both hydrogen gas as well as oxygen gas in a 2:1 volume ratio. In Figure 1a, taken from the OSHA report for Powell Water Treatment, shows this stoichiometric oxygen hydrogen mixture bubbling from the electro-coagulation cell during operation. Arsenic and other materials can also deposit on the cathode of the electro-chemical cell requiring cleaning with sulfuric acid. The use of reactive hydrogen from sulfuric acid under this condition is likely to lead to release of arsine gas. Residual sulfuric acid during the subsequent electro-coagulation operation likely intensified to some extent the release of arsine gas on January 21, 2005.



Figure 1. Electro-coagulation cell showing bubbles of oxygen and hydrogen in a stoichiometric mixture being produced from the electro-coagulation cell.

On January 21, 2005 at the Maineville Ohio location of SUMCO an electrocoagulation unit built by Powell Water Manufacturing was being adjusted by two workers from Powell, Dennis Rasmussen and Dan Smith and two employees of SUMCO,

Bill Wheeler and Jim Crutch. Figure 2 shows the general position of the SUMCO and Powell employees with Dennis Rasmussen and Jim Crutch on a platform holding the electro-coagulation cell and Dan Smith and Bill Wheeler below at floor level running a control board for the electro-coagulation cell. The electro-chemical cell was producing three gasses of interest, hydrogen, oxygen and arsine in order of their production rate with hydrogen at a 2 to 1 ratio with oxygen and arsine at an unknown production rate but well above toxicity limits. Under normal operation the lid to the electro-chemical cell was closed presenting what would appear to be an explosion hazard in the absence of ventilation for the electrochemical cell (Figure 1 b). When the lid is opened, Figure 1a, hydrogen, being lighter than air, rose to the ceiling. Oxygen is just heavier than air so that oxygen pooled in the vicinity of the platform while arsine is much heavier than air and was possibly first lifted in a kind of fountain effect by the hydrogen flow just to the height of Mr. Rasmussen and Mr. Crutch on the platform who reported smelling garlic odor after the exposure. Arsine then separated from the hydrogen flow and fell to the floor below the platform; spreading across the relatively wide floor area in the shed. This prevented further exposure of the two workers on the lower level, Mr. Smith and Mr. Wheeler. Residual arsine on the floor decomposed due to exposure to water, organics and oxygen to As₂O₃ or As₂O₅ and other compounds and complexes of arsenic [Pantsar-Kallio M, Korpela A Analytica Chimica Acta 410 65-70 (2000)]. Some of the arsine gas may have dissipated to the environment though the shed was well sealed due to cold temperatures outdoors.



Figure 1. Schematic of electro-coagulation Device. Two on the platform were Dennis Rasmussen and Jim Crutch. Two on the bottom near the control box were Dan Smith and Bill Wheeler. The safety interlock on the lid to the electrochemical cell was overridden.

The specifications for the electro-coagulation unit as detailed in the OSHA report on Powell were to "... make arsenic separable from water, like water tested on April 23, 2003, at a minimum of 90% removal, when operated according to the manufacturer's instructions." In addition to this information we are aware that Powell knew of the production of hydrogen and oxygen in the electro-chemical cell from their patents and patents cited in their patent litigation.

Summary of Two Powell Patents and Related Literature:

Powell has two patents related to the electro-coagulation device and no other publications pertaining to this field. 6,488,835 (2002) and 6,139,710 (2000) both listing Scot Wade Powell as the inventor.

1) It seems that Powell did not anticipate the production of Arsine in their unit despite indications in the literature [for instance Pinisakul A, Polprasert C, Parkpian P, Satayavivad J, *Water Science and Technology* **46** 247-54 (2002) and papers cited in the OSHA report] and common logic.

2) Powell did anticipate the production of hydrogen gas. This was not considered to be a hazard by Powell despite obvious problems with flammability and explosion hazards as well as clear indications in the literature that the presence of dissolved arsenic and reactive hydrogen presented a serious danger in terms of the highly reactive, flammable and toxic arsine gas.

3) Powell's patents, 6,139,710 and 6,488,835 discuss the sealed tank and the presence of hydrogen gas that is vented to the atmosphere.

4) The patents also discuss the removable sealed lid on the electro-coagulation tank and mention that its purpose is to prevent liquid loss from the tank not necessarily to contain the hydrogen and oxygen gas.

5) The patents discuss the use of evacuated and pressurized tanks but not for the purpose of prevention of exposure to gaseous byproducts. Based on their patent publications Powell seems to be completely blind to problems associated with arsine poisoning.

6) One of the patents cited in the Powell patent pertains to treatment of water contaminated with gallium arsenide from wafer polishing using electro-coagulation, 4,623,436. This patent doesn't mention hazards. The operation in US 4,623,436 occurs in a pressure vessel and the release of pressure is used to cause the coagulated metals to flocculate in a single step of the process rather than producing large amounts of foam throughout the electrolysis.

Summary: Powell knew that gasses were produced in the process and had considered venting of these gasses to the atmosphere in their patents. Powell knew that much of the gas produced was hydrogen. Production of hydrogen and oxygen in a mixed gas stream in an enclosed space from an electrochemical cell which is designed to split water into a stoichiometric mixture ideal for combustion/explosion is usually viewed as an explosion hazard, that is when the lid to the electro-coagulation unit was closed in normal operation the device was an explosion hazard. Powell also ignored the possibility of arsine production in the presence of reactive hydrogen which is well known in the industrial waste-water treatment industry. A simple look at common hazards associated arsenic, for which Powell was contracted to remove, would reveal that arsine production in the presence of obvious concern in this device. It may be that an accident was avoided, in previous applications of similar devices by Powell,

since adequate ventilation was serendipitously provided, i.e. the device was housed outdoors, and because ignition devices were coincidentally never near the explosive hydrogen/oxygen mixtures.

The absence of a hydrogen sensor on the device and the lack of warning signs concerning ignition devices in the vicinity of the electro-coagulation unit is clearly a failure to consider industry standards in the design and manufacture of the electrocoagulation unit, particularly standards for industrial safety. This is also a failure to use common logic and reasonable concern for those involved in the use of this device. A hydrogen sensor would have coincidentally prevented the exposure of Mr. Crutch and Mr. Wheeler to the injuries on Jan. 21, 2005. Elevated hydrogen levels would have been directly associated with the presence of arsine gas since it is produced by reactive hydrogen and arsenic in the electrochemical cell and because hydrogen bubbling up out of the cell served as a carrier gas actually enhancing the fountain effect that lead to the high exposure of Mr. Rasmussen and Mr. Crutch. Powell's employee Mr. Rasmussen clearly failed to meet industrial standards for safety which directly resulted in the exposure both of himself and of Mr. Crutch and Mr. Wheeler to arsine gas. The actions of Mr. Rasmussen combined with a lack of adequate warning signs on the device and the failure to include in the design even the most rudimentary sensors for hydrogen production directly lead to this easily avoidable exposure.

Further, it is common practice to consider the likely reactive pathways associated with toxic metals in electrochemical removal so that the failure to consider the production of arsine gas in the presence of reactive hydrogen in this device reflects a failure to recognize industry standards in design and manufacture of the electro-coagulation unit. If a reasonable design approach had been taken, the device would have included several hydrogen sensors and at least one arsine sensor located in the coagulation unit which should have been equipped with a fail safe shutoff for the unit if arsine gas were detected. This could have been easily accomplished with a simple electrical switch triggered by the sensors. The absence of these simple safety features lead directly to a life-threatening situation for the employees of both Powell and SUMCO.

As an example of current knowledge in the field, Table 1 shows the published results of the 2002 study of an electro-coagulation unit by Pinisakul A, Polprasert C, Parkpian P, Satayavivad J, *Water Science and Technology* **46** 247-54 (2002). Note that this and other literature citations indicate that a large fraction of the arsenic removed is expected to be released as arsine gas. Also it should be noted that the 1 % absorbed to the electrodes would be released as arsine gas in the acid cleaning step of the operating procedure for the Powell device as is documented in several OSHA reports including DHHS NIOSH Pub No79142_32 (1979).

As in various parts	% of As
As incorporated in and adsorbed on the precipitated ECP sludge	64.9-94.9
As as AsH _a gas	10.5–15.6
As adsorbed on the electrode plates and reactor walls	0.03-1.1
Residual As in supernatant	0.2-0.4
Unaccounted As	1.2-19.8

Table 1 Mass balance for As removal in the electro-coagulation (ECP) process.

In addition to what can be clearly determined by an inspection of the purchase order for the electro-chemical cell, a tour of the facility in January 2007 and Powell's web page and published patents, the results of the two OSHA investigations concerning SUMCO and Powell can be considered.

Summary of OSHA Reports:

NIOSH Publication No 79-142 (1979), avaiable on-line, describes steps that should be taken when arsenic and nascent hydrogen (electrochemical or from acid) might come in contact. The publication includes many examples where arsine led to poisoning in the workplace. No specific examples of electro-chemical cells are given, though the publication, if it had been read by Powell, would have clearly indicated the potential for arsine production in the electro-coagulation unit.

A number of cases of arsine poisoning in the lead acid battery manufacture industry are pertinent to this case since these associate trace amounts of arsenic in lead to the electro-chemical production of nascent hydrogen. These are presented in a section beginning "ARSINE CASRN: 7784-42-1" beginning on page 7 of this section. Under the subsection "Probable Routes of Human Exposure:" Accidental exposure from lead-acid batteries is also noted during charging and discharging of the batteries especially when overcharged. There are strong similarities between these electro-chemical cells and the electro-coagulation unit of Powell.

OCCUPATIONAL EXPOSURE: INDUSTR LEAD-ACID BATTERY (5 KWHR) HAS BEEN FOUND TO GENERATE SIGNIFICANT AMT OF STIBINE & ARSINE DURING EQUALIZATION & OVERCHARGE. [VARMA R ET AL; REPORT, ISS ANL/OEPM-78-4 31pp. (1979)]**PEER REVIEWED** OCCUPATIONAL EXPOSURE: IN AN EVALUATION OF CHRONIC OCCUPATIONAL EXPOSURE TO ARSINE, AN EPIDEMIOLOGIC SURVEY WAS CONDUCTED AT A LEAD-ACID BATTERY MANUFACTURING PLANT. **ARSINE** IN 177 BREATHING-ZONE AIR SAMPLES RANGED FROM NONDETECTABLE TO 49 UG/CU M. THE HIGHEST LEVELS WERE FOUND IN THE BATTERY FORMATION AREA, WHERE **ARSINE** IS GENERATED BY THE REACTION OF BATTERY ACID WITH LEAD-ARSENIC ALLOY. **ARSINE** LEVELS ABOVE 15.6 UG/CU M WERE ASSOCIATED WITH URINARY ARSENIC CONCN IN EXCESS OF 50 UG/L (0.67 UMOL/L). IT WAS CONCLUDED THAT THE CURRENT **ARSINE** EXPOSURE STANDARD, 200 UG/CU M, FAILS TO PREVENT CHRONIC INCREASED ABSORPTION OF TRIVALENT ARSENIC FROM THE INHALATION OF **ARSINE**. [LANDRIGAN PJ ET AL; SCAND J WORK ENVIRON HEALTH 8 (3): 169-77

(1982)]**PEER REVIEWED**

Occupational exposure to arsine is possible during manufacture and use in the electronics industry. Exposure is also possible in certain metallurgical processes and in lead/acid battery manufacturing. ...

[Santodonato J et al; Center Chem Haz Assess Report No. SRC-TR-84-728 33 pp. (1985)]**PEER REVIEWED**

OCCUPATIONAL EXPOSURE: IN AN EVALUATION OF CHRONIC OCCUPATIONAL EXPOSURE TO ARSINE, AN EPIDEMIOLOGIC SURVEY WAS CONDUCTED AT A LEAD-ACID BATTERY MANUFACTURING PLANT. **ARSINE** IN 177 BREATHING-ZONE AIR SAMPLES RANGED FROM NONDETECTABLE TO 49 UG/CU M. THE HIGHEST LEVELS WERE FOUND IN THE BATTERY FORMATION AREA, WHERE ARSINE IS GENERATED BY THE REACTION OF BATTERY ACID WITH LEAD-ARSENIC ALLOY. **ARSINE** LEVELS ABOVE 15.6 UG/CU M WERE ASSOCIATED WITH URINARY ARSENIC CONCN IN EXCESS OF 50 UG/L (0.67 UMOL/L). IT WAS CONCLUDED THAT THE CURRENT **ARSINE** EXPOSURE STANDARD, 200 UG/CU M, FAILS TO PREVENT CHRONIC INCREASED ABSORPTION OF TRIVALENT ARSENIC FROM THE INHALATION OF **ARSINE**. [LANDRIGAN PJ ET AL; SCAND J WORK ENVIRON HEALTH 8 (3): 169-77 (1982)]**PEER REVIEWED**

The OSHA report includes several Arsine detectors that are commercially available and can alert to concentrations as small at 0.01 ppm.

1) TG-KA Seris from CEA Instruemnts Inc. model TG-5000KA for Phospine, Arsine, Germane and Silane.

2) The Spectrum Series personal gas detectors from ENMET Corporation that can detect 0.05 ppm Arsine;

3) Bionics Instrument Company Model TG 4000 that can detect 0.2 ppm arsine;

4) The STX monitoring system from PureAire Monitoring systems;

5) Scott Instruments also offers an arsine monitor.

Although cleaning of the electro-coagulation unit with sulfuric acid probably resulted in the production of arsine gas, the cleaning was not performed under conditions that lead to the severe poisoning seen on January 21, 2005. Also, the addition of 1 liter of ferrous sulfate solution probably had little effect on the copious production of arsine gas on January 21. Ferrous sulfate most likely enhanced the precipitation of iron (III) arsenic complexes.

In the OSHA Reports SUMCO was fined \$6,000 and removed the electro-coagulation unit from operation.

Citation 1 Item 1 is a serious violation of 29 CFR 1910.134 (d) (1) (iii) for not identifying and evaluating a respiratory hazard in the work place. Arsine monitors should have been used. Original penalty \$4500

Citation 1 Item 2a Serious violation of 29 CRF 1910.1000(a)(2) Over exposure to Arsine gas. Original penalty \$4500

Citation 1 Item 2b Serious violation of 29 CRF 1910.1000(e) No Gas capturing ventilation, real time monitor for arsine or removal of water off site. The last was apparently chosen. No cash penalty.

Total SUMCO penalties \$9000.

This was negotiated to \$6,000 but most of these negotiations are not clear due to deleted parts of the record.

Powell paid a total of \$2500 for 3 violations and purchased an Arsine detector

Citation 1 Item 1 Serious violation of 29 CFR 1910.134 (d)(1)(iii) arsine gas detectors were needed for testing and manipulation of the electro-coagulation system.

Original penalty \$1500

Citation 1 Item 2a Serious violation of 29 CFR 1910.1200(h)(1) Training was not provided on the handling of arsenic solutions and the potential of producing arsine gas in the presence of reactive hydrogen.

Original penalty \$1500

Citation 1 Item 2b Serious violation of 29 CFR 1910.1200(h)(3)(ii) health hazards of arsine gas were not explained to the workers.

Several labeling issues including training of workers were cited with no Penalty.

Powell was cited for the exposure to arsine gas under a serious violation of 29 CFR 1910.1000(a)(2)

Original penalty \$1500

Powell was also cited for lack of ventilation and the lack of an arsine gas monitor-alarm system.

Total fines for Powell amounted to \$4500 but this was negotiated to \$2500 again in the missing parts of the document.

The most interesting and pertinent part of the two OSHA reports is the Narrative in the Powell report. In this section the officer gives a summary of his impression of the accident which basically lays all of the blame on Powell. This summary of the accident titled "Narrative relating to inspection # 308510288: Powell Water Manufacturing Corporation" describes OSHA's feeling that the accident was chiefly Powell's responsibility "In regard to potential citations, it seems that Powell should be the primary recipient." The narrative also mentions the danger associated with the use of sulfuric acid to clean the electro-coagulation unit between electrolysis treatments due to the well documented hazards associated with arsine production. OSHA is particularly sensitive to this since there are many incidences of cleaning arsenic with acid that have lead to deaths in the work place. Similarly, there have been some cases of alkaline formation of arsine though this seems less well defined or reported in the literature.

The *Narrative* mentions the Kaspar Company of Shiner, Texas and a phone conversation with Paul Markovsky who is an Applications Engineer and Chemist. This is the strongest evidence against Powell since Markovsky describes the Powell process and technique to be "...asking for trouble..." when discussing arsine formation. It is my opinion that the arguments of Markovsky reported in the OSHA *Narrative* are convincing. The use of acid in combination with arsenic should have sent a red flag to any trained technician in the waste water treatment field familiar with arsenic removal. Further, for workers experienced in the use of electrolysis for such waste water treatment several red flags should have at least lead to the use of an arsine sensor for their own personnel safety. The *Narrative* ends by chastising Powell "...*it seems Powell never bothered to spend much time thinking about hazards*... (of) ... *arsenic*..."

Pictures and Diagrams from the OSHA Report:









Pictures from January 5, 2007





