SODIUM BOROHYDRIDE REDUCES HAZARDOUS WASTE

Marilyn J. Lindsay, Chemist I
Matthew E. Hackman, Technical Service Representative
Morton Thiokol/Ventron Division
Danvers, Massachusetts 01923
Russell J. Tremblay, Engineer
Sanders, Inc.
Manchester, New Hampshire 03103

INTRODUCTION

In early 1984, the Ventron Division of Morton Thiokol, Inc. contacted various printed circuit board (PCB) facilities to discuss their waste treatment needs and to promote VenMet™ solution (a stabilized caustic solution of sodium borohydride) [1] as a viable method for removing dissolved metals from printed circuit board manufacturing wastes. Many of these facilities already had segregated treatment systems in place for chelated and non-chelated wastes and were operating consistently below discharge requirements for copper and other metals subject to limitations. At one site, increasing plant production rates were resulting in hydraulic and sludge overloading that approached system capacity. Further increases in plant production could not be considered without taking specific measures to increase waste treatment capacity. As an added result, many concentrated wastes were drummed for offsite treatment or disposal.

The PCB industry has responded favorably to sodium borohydride ($NaBH_4$) technology [2]. Early lab testing on chelated wastes clearly showed dramatic sludge reduction in comparison to the conventional ferrous sulfate ($FeSO_4$) systems. However, early tests also showed unreliable chemical efficiency, copper redissolving problems and unstable flocculation. In response to these initial drawbacks, new methods of using sodium borohydride were developed, evaluated and then tested on actual plant solutions.

CASE STUDY

At the PCB manufacturing site chosen for a full scale trial, the waste treatment facility was operating at its maximum. Both the in-line clarifier and filter press were at full capacity and concentrated liquids had to be drummed for offsite treatment or disposal. If plant production at this facility were to increase, major changes would be required in the waste treatment facility.

The following requirements were established for evaluating the trial results.

1. *Sludge Volume Reduction* - The VenMet™ system must treat all complexed metal solutions and operate within the existing system's sludge capacities.
2. *Effluent Compliance* - The VenMet system must operate comfortably within existing limits (4.5 mg/l Cu maximum daily average; 2.7 mg/l Cu 4 day average) and establish the capability for meeting future, more stringent, EPA requirements.
3. *Low Capital Cost* - Equipment modifications must be minimal.
4. *Economics* - The VenMet system must operate on a justifiable cost basis.

The primary concern of this PCB manufacturer was to reduce sludge loading in the clarifier and filter press thus increasing the capacity of the waste treatment system to accommodate increases in plant production. A plant trial using the VenMet™ system was proposed for the more difficult to treat chelated waste line.

The personnel involved were confident that a successfully implemented VenMet™ system on the chelated wastes would provide the following: 1) Chemical reduction of dissolved copper to the metallic state at a fraction of the sludge volume generated by the existing $FeSO_4$ based system; 2) Increased waste treatment system capacity; 3) Dependable copper removal to below 1 mg/l; and 4) Reduced chemical handling for operators.

The initial comparison of the VenMet system costs vs. the $FeSO_4$ system costs was not clearly favorable. However, marginally increased operating costs were acceptable to the manufacturer if the waste treatment system capacity could be increased without requiring substantial capital cost.

INITIAL SYSTEM DESIGN

The $FeSO_4$ system was typical of many chelated copper systems used in PCB manufacturing waste treatment (See Figure 1). The process consisted of two reaction stages, a flocculation step, clarification and final filtration. In the first stage reaction tank, the pH was controlled at 2-3 and a 0.7% $FeSO_4$ solution was added generally with a 14 to 1 iron to copper ratio. The waste solutions then overflowed by gravity into the second tank. Here the pH was raised to 8.5-9.0 with 25% caustic solution resulting in a ferric hydroxide-cupric hydroxide precipitate. Anionic polymer was added in a flash-mix stage immediately before the clarifier to improve flocculation.

Residence times for the different reaction steps were 20-40 minutes in the first and second tank and 5-10 minutes in the flash-mix stage. The clarifier was sized for 1-1.5 hours of retention and dual, parallel, cross-linked sand filters removed any floc carryover from both the chelated and a second non-chelated system. Sludge from the clarifiers was sent to a holding tank for further dewatering.

SYSTEM MODIFICATIONS AND OPERATION

The conversion of the $FeSO_4$ system to the VenMet™ system was simple and straightforward (See Figure 2). Key engineering considerations were: 1) Adequate residence time for chemical reactions and flocculation; 2) Thorough mixing; 3) Accurate and stable process control (both pH and ORP); and 4) Good flocculation and settling.

With the exception of an ORP control function, all of these elements were provided in the original system. To implement the VenMet system, the pH control point in the first reaction tank was changed from 2-3 to 6. A 10% solution of sodium bisulfite ($NaHSO_3$) was substituted for the $FeSO_4$ solution. The $FeSO_4$ make-up tank and feed pump were used without any changes although materials of construction had to be checked for compatibility.

Modifications to the second reaction tank included: conversion of the pH controller to ORP control; replacement of 25% caustic feed with a 10% VenMet™ solution; and addition of a cationic polymer. Output of the ORP controller adjusted the metering pump rate for the dilute VenMet solution. A different anionic polymer was selected for improved flocculation and was added in the flash-mix stage in place of the original anionic polymer. This was the extent of the operational changes required for the conversion.

The initial ORP control was set at −800mV, which resulted in VenMet solution feed at approximately 10 times the stoichiometric requirement [3]. The initial $NaHSO_3$ feed was set at an approximately 15:1 ratio of $NaHSO_3$ to copper. Cationic and anionic polymers were added at 30 and 5 mg/l, respectively, based on previous flocculation studies.

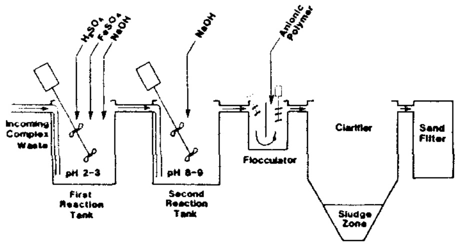

Figure 1. Original ferrous sulfate system.

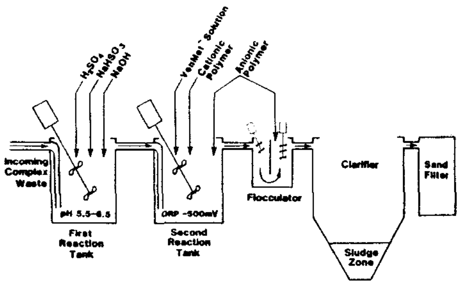

Figure 2. Existing VenMet system.

VenMet™ CHEMISTRY

VenMet solution is an effective reagent for the reduction of metal cations from industrial waste streams [2,4]. Sodium borohydride has a reducing capacity of 8 electrons/mole or an equivalent weight of 4.75 g/molar electron and a standard electrochemical potential of −1.25 volts.

In the first stage of the VenMet™ process, a 10% solution of sodium bisulfite is prepared by adding sodium metabisulfite powder to a dilute caustic solution. The addition of caustic is necessary to prevent the bisulfite from driving down the pH and giving off SO_2 gas. This solution has an ORP of approximately −200 mV and is added to the incoming waste stream at a pH of 6-7. The bisulfite reduces or neutralizes any oxidizing agents in the waste stream (i.e., persulfate, permanganate, peroxide and/or oxygen) but does not reduce the metal cations present.

$$HSO_3^- + S_2O_8^{2-} + 2\,OH^- \rightarrow 3\,SO_4^{2-} + H_3O^+ \qquad (1)$$

$$3HSO_3^- + 2\,MnO_4^- \rightarrow 3SO_4^{2-} + 2\,MnO_2 + H_3O^+ \qquad (2)$$

$$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H_3O^+ \qquad (3)$$

In the second stage, VenMet™ solution (diluted 1 part VenMet solution to 10 parts water) is added. Dilution allows for faster mixing and improves the reaction especially with low level copper concentrations. Dilution of VenMet solution also helps to prevent over-dosing which can result in the formation of small hydrogen gas bubbles that can disturb flocculation and settling.

Sodium borohydride reacts with any residual bisulfite from stage one to form sodium dithionite.

$$8NaHSO_3 + NaBH_4 \rightarrow 4Na_2S_2O_4 + NaBO_2 + 6H_2O \qquad (4)$$

The dithionite provides further neutralization of oxidizing agents left in the stream and partially reduces metal cations.

$$S_2O_4^{2-} + S_2O_8^{2-} + H_2O + OH^- \rightarrow 2SO_3^{2-} + 2SO_4^{2-} + 3H^+ \qquad (5)$$

$$Na_2S_2O_4 + 2Cu^{2+} + 2H_2O \rightarrow 2Cu^+ + 2NaHSO_3 + 2H^+ \qquad (6)$$

The oxidation of dithionite regenerates bisulfite which in turn maintains a mildly reducing environment that stabilizes the precipitated copper.

While the mechanism of sodium borohydride reduction is not fully understood in this system, we believe that the Cu^{2+} is reduced through a Cu^+ species to give Cu°. As the Cu^{2+} is reduced to Cu^+, the chelate to metal bond is broken thus promoting rapid reduction to the metallic state.

$$NaBH_4 + 8Cu^+ + 2H_2O \rightarrow 8Cu^\circ + NaBO_2 + 8H^+ \qquad (7)$$

The results are a dense, compact metallic sludge and an effluent typically less than 1 mg/l Cu. The sludge from the borohydride reduction is then easily dewatered to 55% TS average containing greater than 80% Cu (on a dry weight basis). The ferrous sulfate sludge is dewatered to 35% TS average containing less than 5% Cu which is less favorable than the borohydride sludge.

A binary flocculation system is used to improve solid/liquid separation. A cationic polymer, generally a polyamine, is added in stage two and an anionic polymer, usually a hydrolyzed polyacrylamide, is added to a flash mix tank just prior to the clarifier. It is critical to get proper dosage levels and mixing when using flocculating aids. Over-dosing as well as under-dosing polymers can cause dispersion of particles instead of agglomeration.

KEY PROCESS CONSIDERATIONS

The major considerations for implementing VenMet™ solution in a waste treatment system include:

1. *pH Control* - good control is paramount for effective and consistent chemical reduction.
2. *Residence Time* - a 20-30 minute reaction time is necessary to assure complete chemical reduction under controlled process conditions. Generally, lower pH reduces retention requirements and higher pH increases it.
3. *Flocculation* - The VenMet™ system does not add appreciable solids to the waste treatment process which may adversely affect flocculation. A binary flocculation system is generally used when implementing sodium borohydride in these systems.
4. *Prereduction Chemistry* - Extensive lab testing showed that $NaHSO_3$ was necessary to lower VenMet

system chemical requirements and to stabilize the resulting metallic precipitates as discussed in the *Chemistry* section.

5. *Final Filtration* - Because of flocculation problems encountered during start-up and the clarifier not being designed for the reduced solids levels, a final sand filter was necessary to ensure acceptable effluent quality.

OPTIMIZATION

During start-up and subsequent operation, several changes were made to improve performance (See Figure 2).

The pH set point in the first reaction tank was lowered from 6.0 to 5.5. This accelerated the VenMet system reaction with minimal hydrolysis due to the good mixing conditions.

$NaHSO_3$ usage was optimized in conjunction with $NaBH_4$ to maximize copper removal and minimize flocculation and settling problems. When the $NaHSO_3$ dosage is too low, a sludge stability problem occurs and when the dose is too high, a very fine, pin floc is formed which is difficult to coagulate.

Very low incoming copper levels (below 20 mg/l) increased settling and clarification problems. Concentrated wastes were bled into the continuous treatment system at a constant, uniform rate to maintain minimum copper levels above 20 mg/l. Instantaneous addition would upset the system resulting in incomplete reduction, over consumption of sodium borohydride and poor flocculation and settling. One solution that was encountered in this system was a high pH photoresist stripper solution that was very difficult, if not impossible, to treat and floc. However, when bled into the system at a 0.25 gpm rate, this solution was treated with little disturbance to the system chemistry or flocculation.

The addition of anionic polymer at the flash-mix stage was not efficient due to inadequate retention time. Therefore, anionic polymer was added to the second reaction tank along with the addition at the flash-mix stage. This provided extended retention and mixing time for the anionic polymer.

COST COMPARISON

The data in Table I represent a sixty day work period for both chelated and non-chelated waste systems. Shown is a cost comparison of the conventional ferrous sulfate system vs. the VenMet™ system. Included for both cases is the cost of the non-chelated waste treatment which is assumed to be constant in each case.

VenMet system shows an overall cost decrease of 12% per day or approximately $10,000.00/ year.

Combined sludge generation (chelated and non-chelated) decreased 66%.

Sludge generation from the chelated waste stream alone decreased 82%.

Table I. Cost Comparison Data

Ferrous Sulfate System	per 60 days	approximate cost
ferrous sulfate	20,000 lbs	$ 2,300.00
sodium hydroxide	12,000 gal	4,000.00
sulfuric acid	400 gal	530.00
flocculants	15 lb	21.00
	Chemical cost per 60 day	$ 6,851.00
	Chemical cost per day	$ 114.00
	Sludge handling cost per day	$ 215.00
	Total Cost Per Day	$ 329.00
VenMet™ System	per 60 days	approximate cost
VenMet™ solution	186 gal	$ 6,000.00
sodium hydroxide	7,500 gal	2,400.00
sulfuric acid	330 gal	390.00
sodium bisulfite	13,000 lbs	3,700.00
flocculants	27.7 gal	444.00
	Chemical cost per 60 day	$12,934.00
	Chemical cost per day	$ 215.00
	Sludge handling cost per day	$ 74.00
	Total Cost Per Day	$ 289.00

VenMet system shows an overall cost decrease of 12% per day or approximately $10,000.00/year.

SUMMARY

Sludge reduction was a major goal at this facility. The clarifier could not accommodate the solids loading from the $FeSO_4$ system resulting in costly, continuous operation of the filter press. With essentially no additional capital costs, the VenMet™ system was successfully implemented providing effluent copper levels typically less than 1 mg/l. The sludge from the chelated wastes was reduced 82%, and the filter cake dewatered to 55% TS average as compared to 35% TS average with ferrous sulfate. The operation of the filter press was reduced from continuous operation to approximately three times per week and cycle times were cut in half.

As a result of the sludge reduction, sludge disposal costs for the chelated wastes decreased 82% and overall daily operating costs (both chelated and non-chelated) were reduced 12%. Further optimization of the VenMet™ system is expected to yield lower chemical costs. In addition to the above benefits, the copper content of the sludge from the chelated wastes increased from approximately 5% to 80% (on a dry weight basis) rendering the sludge suitable for reclamation and thus reducing, and possibly eliminating, the liability associated with hazardous waste disposal. Once the VenMet system is fully optimized in the chelated waste treatment line, this manufacturer plans to implement VenMet™ solution on the non-chelated waste line. This is expected to yield a similar reduction in sludge volume and further reduce sludge disposal costs.

REFERENCES

1. VenMet™ solution is a stable aqueous solution of $NaBH_4$ containing 12% $NaBH_4$ and 40% sodium hydroxide, a product of MORTON THIOKOL, INC., Ventron Division.

2. (a) "EPA Effluent Compliance and Hazardous Sludge Control with Sodium Borohydride," S. F. Heleba, presented at Massachusetts Hazardous Waste Source Reduction Conference and Exhibition, Boxboro, MA (October 13, 1983) and references therein.

   (b) "Industrial Removal and Recovery of Metals with Sodium Borohydride," E. A. Sullivan, presented at the Third International Meeting on Boron Chemistry, Germany (1976).

   (c) "Control of Heavy Metal Discharge in the Printed Circuit Industry with Sodium Borohydride," J. A. Ulman, presented at the 1984 AES SUR/FIN Annual Technical Conference and Exhibit, New York City (July 1984).

   (d) "Case Histories: Reviewing the Use of Sodium Borohydride for Control of Heavy Metal Discharge in Industrial Waste Waters," M. M. Cook, J. A. Lander, and D. S. Littlehale, *Proceedings of the Industrial Waste Conference,* Purdue University (May 8-10, 1979) Ann Arbor Science Publishers, Inc., Michigan (1980); and references therein.

   (e) "Use of Sodium Borohydride to Control Heavy Metal Discharge in the Photographic Industry," M. M. Cook and J. A. Lander, *J. Appl. Photographic Eng.*, 5 (3), 144 (1979); and references therein.

3. The theoretical requirement of $NaBH_4$ is calculated based on the equation.

$$BH_4^- + 4\,Cu^{2+} + 2\,H_2O \rightarrow 4\,Cu^{\circ} + BO_2^- + 8\,H^+$$

   Theoretical ratio: $BH_4^-/Cu^{2+} = 0.15$ (wt.).

4. (a) "Metal Removal and Recovery with Sodium Borohydride," T. F. Jula, presented at the Institute of Printed Circuits, 1977 Fall Meeting, Chicago (1977).

   (b) R. N. Duncan and J. R. Zickgraf, "One Way to Treat Spent EN Baths," *Products Finishing* (January 1982).

   (c) K. Parker, "The Waste Treatment of Spent Electroless Nickel Baths," presented at the First AES Electroless Plating Symposium, St. Louis (March 1982).

   (d) "Simplifying Heavy Metal Recovery with Sodium Borohydride," T. F. Jula, *Process Eng.* (1975).

   (e) "Sodium Borohydride Environmental Control Applications: Reduction of Nickel(II) Complexes in Spent Electroless Plating Baths," M. E. Fleming and J. A. Ulman, presented at the Electroless Nickel Conference IV, Chicago (April 22-24, 1985).

(f) Morton Thiokol, Inc., Ventron Division Technical Brochures:
- Metal Removal and Recovery with Sodium Borohydride
- Metal Recovery with Sodium Borohydride
- Inorganic Reductions with Sodium Borohydride - Principles and Practices (and references therein)
- Heavy Metal Recovery with Sodium Borohydride
- Sodium Borohydride