PILOT SCALE TESTING OF SOLVATED ELECTRON TECHNOLOGY

Timothy L. Orton, Envirocare of Utah, Inc.
Mack Jones, Commodore Advanced Sciences, Inc.

ABSTRACT

Envirocare of Utah, Inc. (Envirocare), in conjunction with Commodore Advanced Sciences, Inc. (Commodore), has completed pilot scale studies of Commodore's Solvated Electron Technology system. This study was completed to determine the applicability of the Solvated Electron Technology to mixed waste streams arriving at Envirocare's Clive facility. A total of 60.8 pounds (lbs) of a sludge mixed waste stream was treated in five batches during this study. The batches were smaller than usual due to the high moisture content (~75%) of this waste stream. Three analytes of interest (Freon-113, 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE)) were detected in the pre-treatment samples at concentration levels (90% confidence intervals) ranging from 84.9 to 467.1 mg/kg for Freon-113, 111.2 to 413.8 mg/kg for TCA, and 77.1 to 189.3 mg/kg for TCE. Through the treatment process, these analytes were reduced in concentration greater than 99.98% for Freon-113 and TCA, and 99.96% for TCE. Final levels of these three analytes were below their respective Universal Treatment Standards (UTS) of 30 mg/kg, 6 mg/kg, and 6 mg/kg, respectively. 1,4 dichlorobenzene was also treated to non-detectable levels through this process. Additionally, the pre-treatment samples contained lead at a total concentration of 6 mg/kg and a TCLP value of 1.06 mg/l (exceeding the regulatory standard of 0.75 mg/l). Post treatment samples show that the concentration of lead within the waste was also reduced to a total concentration of 3.0 mg/kg and a TCLP value of 0.04 mg/l, an order of magnitude below the regulatory standard. Due to the high moisture content of the waste stream, an extra neutralization step was necessary to assure that the final product was below Land Disposal Restriction (LDR) characteristic waste standards. This neutralization step resulted in the generation of a large amount of water, which then needed to be treated as a mixed waste. This water generation could have been eliminated through the use of different neutralization agents or through pre-treatment of the waste stream.

INTRODUCTION

Waste streams contaminated with organic compounds have proven to be very difficult to treat using conventional stabilization methods. Furthermore, organic contaminants tend to reduce the effectiveness of the treatment methods for the more easily stabilized constituents such as cadmium and lead. The Environmental Protection Agency (EPA) has set land disposal restriction (LDR) guidelines for the trace amounts of organics present within a waste stream. The Code of Federal Regulations (CFR) provides Universal Treatment Standards (UTS) for all organic (and inorganic) contaminants. Specific UTS concentrations in both wastes and wastewasters are provided in 10 CFR 268.48 (1).

Envirocare has become interested in the treatment of organic wastes for the two reasons stated above: (1) LDR guidelines prohibit land disposal prior to treatment to UTS standards and (2) trace organic contaminants tend to inhibit the treatment process for inorganic contaminants. A treatability study was performed at Envirocare to evaluate the applicability of the patented Commodore Solvated Electron Technology (SET) treatment system. At the time of this study, a lead contaminated waste was present on site containing relatively high levels of volatile organics. Conventional treatment methods were not working on this waste stream; therefore, it was considered to be a good candidate waste stream for use in this treatability study.

Chemistry

The SET process uses a phenomenon that has been known to chemists for over 100 years: alkali or alkaline-earth metals dissolved in ammonia form a dark blue solution with powerful reducing properties. The ammonia tends to break down the metal into a positive cation and a free electron. This can be illustrated by the following equation utilizing sodium as the metal:

$$\mathrm{Na}^{0} \xrightarrow{\mathrm{NH_3}} \mathrm{Na}^{+} + \mathrm{e}^{-} \qquad \text{(Eq. 1)}$$

The solvated electron solution destroys halogenated organic compounds by stripping the halogens from the compound, creating a non-hazardous salt and open-ended hydrocarbon monomers that can combine with themselves and/or other compounds within the matrix to create non-hazardous long-chain hydrocarbons. The following two step process is a simplistic depiction of this process illustrating the destruction of a chlorinated hydrocarbon (R) by a sodium induced solvated electron solution:

$$\begin{aligned} &(1) \qquad \mathrm{Na}^{+} + \mathrm{RCl} \longrightarrow \mathrm{NaCl} + \mathrm{R}\cdot \\ &(2) \qquad \mathrm{R}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{R}` \end{aligned} \qquad \text{(Eq. 2)}$$

Furthermore, aromatic compounds such as benzene and toluene are also treated by solvated electrons, following the Birch reduction reaction to form non-hazardous cyclohexadienes (2).

The solvated electron solution preferentially treats first-order kinetic reactions over higher-order kinetic reactions. A first-order kinetic reaction is only dependent upon the concentration of one of the reactants (contaminant or solvated electrons). A second-order kinetic reaction is dependent on both the concentration of the contaminant and the concentration of the solvated electrons. For example, a simple halogenated compound such as chloromethane would be completely treated prior to the electrons attacking a compound such as benzene or, as was observed in this treatability study, carboxilic acids (compounds with the group –COOH attached) and acetone. In order to treat second-order (or higher) reactions, excess reagents (sodium) would need to be added to the system.

One compound of concern that reacts with solvated electrons under first-order kinetics is water. The reaction of sodium with water creates a caustic (sodium hydroxide) and a flammable (hydrogen gas) product and is extremely exothermic, generating large quantities of heat. This reaction is as follows:

$$2\mathrm{Na}^+ + 2\mathrm{H_2O} \longrightarrow 2\mathrm{NaOH} + \mathrm{H_2} \qquad \text{(Eq. 3)}$$

Due to this first-order reaction, it can be reasonably assumed that large quantities of water could inhibit treatment using the SET process. This assumption is significant due to the high moisture content of the waste treated during this treatability study.

TREATABILITY STUDY OBJECTIVES

The objectives of this treatability study include:

- Determine if the RCRA organics within the waste material can be treated below UTS standards utilizing the SET process.
- Confirm that no new listed hazardous compounds are created through the process.
- Determine the effects that excess water within the waste has on the treatment process.

Optimization of the process was not performed during this study.

PROCESS DESCRIPTION

The SET treatment process is a batch operation performed within a completely enclosed system. Figure 1 is a schematic diagram of the equipment utilized in this treatability study. The entire unit consists of six subsystems: a mixer vessel, a SET generation subsystem, an ammonia recovery subsystem, decant tanks, an off-gas scrubber, and a control subsystem. The entire system is loaded on a single skid and was placed within Envirocare's Mixed Waste Operations Building to provide tertiary containment and extra off-gas handling capabilities (baghouse; HEPA and carbon filters).

Treatment takes place within the mixer vessel, which is a horizontal cylindrical treatment cell with a motor-driven centerline shaft and six plow mixers. The vessel contains a top inlet port to introduce the waste material and a bottom drop port to remove treated material. The entire vessel is surrounded by a hot water jacket to aid the post-treatment ammonia recovery process. The outer dimensions of the vessel are three feet in diameter by six feet long with a total volume of approximately 16 ft^3 (~118 gallons). Solid waste is initially loaded into this vessel and mixed with ammonia, which acts as a suspension medium to create a solution amenable to the treatment process.

The next step in the treatment process is to create the solvated electron solution. The solution is created within the SET generation subsystem prior to being introduced into the mixer vessel. The SET generation subsystem consists of a small heat-jacketed sodium tank and a larger solvate (mixing) tank. The solvated electron solution is initiated by melting a specific amount of sodium and mixing with liquid ammonia in the solvate tank. When the solvated electrons are formed, they create a vivid blue solution. Using this attribute, the state of the solvated electron solution may be ascertained by direct observation through the solvate tank viewports. After the solution has been established and has turned blue, it is injected slowly into the mixer vessel using the vapor pressure of anhydrous ammonia. The pressure within the mixer vessel is careful monitored during this process since the reaction is extremely volatile, especially if water is present in the initial waste stream. The reaction is almost instantaneous and therefore is limited by the time it takes to introduce the solvated electron solution into the mixer tank. Upon completion of this transfer, the reaction is complete and the ammonia recovery process may begin.

The ammonia recovery subsystem consists of a hot water heater, an air conditioning refrigeration package, a heat exchanger and an ammonia compressor. The hot water heater heats the water flowing through the jacket of the mixer vessel in order to boil the ammonia from the mixture after the treatment has been completed. The ammonia vapors are condensed within the heat exchanger, using the refrigeration package, and then conveyed into the ammonia holding tank utilizing the pressure difference created by the ammonia compressor. The ammonia recovery step is, by far, the most time consuming step in the treatment process. The residue left within the mixer vessel after the ammonia recovery process is a white, powdery solid material with very little moisture content.

The decant tanks are utilized to manually introduce liquid reagents into, or remove liquid ammonia from, the mixer vessel. These tanks would be used if the decanted ammonia needed a washing step prior to regeneration or, as in this case, they could be used to introduce a neutralizing acid into the system as a post-treatment step.

The system is completely enclosed with all off-gases vented through the scrubber, which consists of a 300-gallon tank, a water recirculation pump, and a counterflow, frit-filled column. The water within the scrubber is slightly acidified with sulfuric acid in order to neutralize any ammonium hydroxide that is formed. The outlet vent from the scrubber was vented directly into the buildings off-gas collection system consisting of a baghouse, HEPA and charcoal filters.

The final subsystem within the unit is the control subsystem. This subsystem is really a separate overall system that monitors all aspects of the treatment process including pressures and temperatures within the various units, conductivity within the mixer vessel, and weights of the reagents. The treatment unit is manually controlled with the control subsystem providing information to the operator.

EXPERIMENTAL

Waste Description

The waste stream utilized during this treatability study was a laboratory mixed waste sludge contaminated with lead and high in RCRA organic compounds. This waste contained the hazardous waste codes F001, F003, F005, and D008. Under current treatment processes at the Envirocare facility, this waste could not be treated to land disposal regulation (LDR) requirements. The waste stream also contained a high water content, approximately 75%. This aspect of the waste was unanticipated prior to treatment and caused some difficulties as explained below.

The waste used for this study was contained in a single 85-gallon overpack. A representative description of the waste was obtained by taking four discrete random samples from the drum and analyzing for volatile organic compounds (VOCs) using SW-846 Method 8260B protocols. An additional sample was taken for an analysis of semi-volatiles (SVOCs) utilizing SW-846 Method 8270C. Only three analytes were detected within all four volatile pre-treatment samples: Freon 113, TCA and TCE. Only one contaminant, 1,4-dichorobenzene, was detected in the semi-volatile analysis. Results of these pre-treatment analyses are tabulated in Table I.

Table I. Pre-Treatment Results

Contaminant (mg/kg)	**Sample Number**				
	1 (VOC)	2 (VOC)	3 (VOC)	4 (VOC)	5 (SVOC)
Freon 113	652	128	280	46.5	-
TCA	574	141	220	115	-
TCE	177	49.6	92.7	86.4	-
1,4 dichlorobenzene	-	-	-	-	15.4

From this data, the 90% confidence interval for the true mean (μ) for each of the three VOCs was calculated to be:

Freon 113: $84.9 \text{ mg/kg} < \mu < 467.1 \text{ mg/kg}$
TCA: $111.2 \text{ mg/kg} < \mu < 413.8 \text{ mg/kg}$
TCE: $77.1 \text{ mg/kg} < \mu < 189.3 \text{ mg/kg}$

Additionally, in the SVOC analysis, the identity and concentration of the 10 highest peaks on the chromatogram was determined. This analysis showed the presence of long-chain hydrocarbons and/or carboxylic acids within the waste matrix. This analysis was necessary for the primary objective to determine if any new hazardous organic compounds were created during the treatment process. This representation is typical (and expected) for this type of material.

Treatability Description

Under normal, dry waste conditions, the mixer vessel would be loaded with 48 pounds of contaminated material for each treatment batch. Approximately 53 pounds (10 gallons) of anhydrous ammonia would be added to the vessel to create the initial treatment slurry. Another 53 pounds of ammonia would be added into the solvate tank and mixed with up to three pounds of metallic sodium to create the solvated electron solution. However, due to the high moisture content within the waste, smaller batches were performed and larger ammonia volumes were used during this treatability study.

During this study, five batches were treated, four with approximately 10 pounds of waste loaded and a fifth with 20 pounds of waste. A total of 60.8 pounds of material was treated. Approximately fifteen gallons of ammonia was added to the waste in each batch to create the treatment slurry. Extra ammonia was added beyond the normal parameters discussed above in order to dilute the moisture content of the waste stream. This slurry was allowed to mix for approximately fifteen minutes before the solvated electron solution was introduced. The solvated electron solution was created by dissolving approximately nine pounds of sodium into 15 gallons of ammonia. The solvated electron solution was slowly added to the treatment slurry with the pressure watched closely. This process took four to six minutes for each batch. Ammonia recovery began immediately after the solvated electron solution was completely added into the mixer vessel and took between five and seven hours to complete.

The treated material was a white powder with a pH around 14 due to the reaction of sodium and water forming sodium hydroxide. Therefore, a post-treatment step was necessary to remove the corrosive characteristic from the treated waste. The treated material was left in the mixer vessel until 20 pounds of waste had been treated, then a neutralizing step was performed using a dilute solution of sulfuric acid. Unfortunately, this step created a large amount of contaminated water due to the reaction between sulfuric acid and sodium hydroxide along with the excess water used for acid dilution. Post-treatment pH was between 7 and 10 for all batches.

Upon completion of the neutralization step, the treated solution was pumped into an 85-gallon overpack, the solids allowed to settle out, and the water decanted off into a second 85-gallon overpack. A total mass of approximately 1000 pounds was produced through the treatment process.

RESULTS AND DISCUSSION

Post-treatment samples were taken at the completion of each batch, prior to the neutralization step. Furthermore, six discrete samples were taken from the solid portion of the treated material: four were analyzed for VOCs using method 8260B, one was analyzed for SVOCs using method 8270C and one sample was analyzed for lead (total and TCLP). Two samples were also taken from the aqueous component and analyzed for volatiles and lead. Results from the individual post-treatment samples are provided in Table II and the organic results from the treated solid material are given in Table III.

Table II. Post-Treatment Sample Results

Contaminant (mg/kg)	**Sample Number**				
	Post 1	Post 2	Post 3	Post 4	Post 5
Freon 113	ND	ND	ND	ND	ND
TCA	ND	ND	ND	ND	ND
TCE	ND	ND	ND	0.06	ND
1,4 dichlorobenzene	0.1	0.2	0.2	0.2	0.3

Table III. Results for the Treated Solid Material

Contaminant (mg/kg)	**Sample Number**				
	1 (VOC)	2 (VOC)	3 (VOC)	4 (VOC)	5 (SVOC)
Freon 113	ND	0.14J	ND	ND	-
TCA	ND	0.073J	ND	ND	-
TCE	ND	0.07J	0.058J	ND	-
1,4 dichlorobenzene	ND	0.074J	ND	ND	ND

The method detection limits (MDLs) for the volatiles analyses were 0.06 mg/kg for Freon 113, 0.04 mg/kg for TCA, and 0.05 mg/kg for TCE and 1,4-dichlorobenzene. The MDL for 1,4-dichlorobenzene in the semi-volatile analysis was 1.0 mg/kg. A "J" value within the tables indicates that the compound was detected above the MDL but was below the practical quantitation limit (PQL). The UTS concentrations for each of these compounds are: 30 mg/kg for Freon 113, 6.0 mg/kg for TCA, 6.0 mg/kg for TCE, and 6.0 mg/kg for 1,4-dichlorobenzene. All contaminant concentrations within the treated waste were well below these limits.

The results show removal efficiencies of greater than 99.98% for Freon 113 and TCA and greater than 99.96% for TCE. In addition, the process also had a removal efficiency of greater than 99.67% for 1,4-dichlorobenzene. This confirmed the first objective, that the SET process effectively treated the RCRA organics below LDRs.

Acetone was also detected in all four of the samples at concentrations ranging from 0.3 to 2.1 mg/kg. It was originally postulated that acetone was being formed throughout the process; however, this theory was rejected upon examination of the method detection limits utilized between the pre- and post-treatment samples. Since the post-treatment samples contained much smaller concentrations of the contaminants of interest, they were diluted to a much greater dilution factor than the pre-treatment samples and subsequently had a much lower MDL.

No compounds were detected in the post-treatment SVOC analysis. However, an examination of the ten highest peaks on the chromatogram was also performed with this sample. This analysis showed that all of the smaller (<10 carbon) compounds that were found in the pre-treatment sample had been eliminated from the matrix, leaving long-chain carboxylic acids. This is consistent with the chemical theory behind the SET treatment process since hydrocarbon monomers are created within the system and readily combine with themselves and/or other compounds within the matrix. Thus, it was expected to find longer chain hydrocarbons in the post-treatment analysis than were initially present prior to treatment. The carboxylic acids, which were found in both the pre- and post-treatment samples, were not attacked by the solvated electrons. This is also expected since treatment of carboxylic acids requires the breaking of a double bond, which is second-order kinetics and, as explained above, the solvated electrons preferentially attack the first-order kinetic molecules. None of these detected compounds were listed RCRA hazardous compounds; therefore, the second objective was verified.

Previous work by Commodore has indicated that halogenated hydrocarbons react with solvated electrons at a rate several orders of magnitude faster than with water. Since a stoichiometric quantity of sodium was calculated for treatment and utilized in the batches of this treatability study, the previous work could be verified by doubling the size of the batch while maintaining the original quantity of sodium. This crude experiment was performed in the third batch of this treatability study. During the treatment of this batch, none of the operating parameters changed markedly from the other batches. Furthermore, the results for Post 3 in Table II show that treatment of the target analytes was still attained utilizing one-half of the stoichiometric quantity of sodium. Therefore, as expected, the sodium reacts with the halogenated materials preferentially to reacting with the water. Further experimentation would be necessary to ultimately prove this theoretical point. This experiment verified the third objective and provided proof that water within the waste stream did not adversely affect the treatment process.

Prior to treatment, lead was found within the waste at approximately 6 mg/kg and TCLP results yielded 1.06 mg/l leached from the sample. The UTS for lead is a TCLP less than 0.75 mg/l, therefore treatment was necessary. The post-treatment analytical results yielded a lead concentration of 3.02 mg/kg within the solid portion of the treated material. A TCLP analysis was also performed on the post-treatment sample and yielded a value of 0.04 mg/l, an order of magnitude lower than the regulatory limit. Solvated electrons do not react with lead so it was assumed that the lead adhered to the fines in the water matrix or was solubilized in the water itself. However, lead was not found at detectable levels (0.02 mg/l) within the waste water. This is most likely due to dilution within the amounts of water utilized (> 100 gallons) during the neutralization process. An analysis for lead was not performed on samples taken prior to the neutralization step.

The water samples were analyzed for VOCs using method 8260B at two different dilution ratios. Results from these analyses are tabulated in Table IV.

Table IV. Post-Treatment Water Sample Results

Contaminant (mg/l)	**Sample 1**		**Sample 2**		**UTS**
	Conc.	**MDL**	**Conc.**	**MDL**	
Freon 113	ND	0.100	ND	0.040	0.057
TCA	ND	0.010	ND	0.004	0.054
TCE	ND	0.015	ND	0.004	0.054
Acetone	5.01	0.200	0.802	0.080	0.28
Acetonitrile	ND	0.150	0.930J	0.060	5.6
2-butanone (MEK)	ND	0.035	0.160J	0.0014	0.28

The three contaminants of interest were below detection levels and therefore well below their respective UTS levels as provided in Table IV. However, three compounds are showing up in the water samples that were not present (at detectable levels) within the solid pre- or post-treatment samples. Acetonitrile and 2-butanone do not pose a problem since their concentrations are below their respective UTS levels. Acetone is a problem since the concentration found within the wastewater is greater than the UTS wastewater standard. The acetone was stripped from the waste material and dissolved into the aqueous solution. Since the treatment of acetone would follow second-order kinetics, it was not treated, but simply transferred from the solid to the liquid phase. Acetone was found in the post-treatment analytical samples taken before the neutralization step at concentrations ranging from 1.5 to 5.7 mg/kg.

This brings up a fundamental problem that occurred during this treatability study: an extra waste stream was created (water) that acted as a transfer medium for contaminants. The creation of water caused many problems and extra costs to the treatment process: an extra waste stream was created that then needed treatment, an extra analytical analysis was necessary, extra waste handling was performed, individual batches were smaller than usual, etc. The generation of this water could have been minimized, or avoided altogether, if better forethought was put into the treatment process. The most obvious solution would have been to add a pre-treatment drying step to the waste. This is what Commodore usually does for wet waste streams; however, since this situation was not anticipated, the drying equipment was not brought on-site with the rest of the treatment process. Another possible solution could have been a better choice and/or method of neutralizing the post-treatment material. A majority of the water introduced into the system was through the acid dilution process. A more concentrated acid solution would have introduced much less water to the process. In order to utilize a less dilute acid, it would have been preferential to use an acid more amenable to this neutralization process. Concentrated phosphoric acid would have been a good choice for a neutralizing acid since extra dilution water would not be added to the system. An even better choice of neutralizing agent could have been solid ammonium chloride. This material could have been introduced into the system prior to the ammonia recovery step, neutralized the sodium hydroxide, and become part of the ammonia recovery process with the addition of very little water to the system. If this last approach were utilized, the final product would have consisted of a very dry material. Other potential solutions are available and more work may be performed in this area to arrive at an optimized neutralizing agent and/or method.

CONCLUSIONS

The Commodore Solvated Electron Technology successfully treated approximately 60 pounds of a mixed waste stream contaminated with lead and high in RCRA organic compounds. All organic compounds were treated to less than the regulatory limits for land disposal. Furthermore, the concentration of lead in the post-treatment solid residue was approximately 50% of the initial concentration and passed the TCLP test by an order of magnitude over regulatory levels. Therefore, the treated solid residue from this process could be directly disposed in Envirocare's Mixed Waste Landfill.

The treated waste stream was a laboratory sludge containing large quantities of water (~ 75%). The water within the sludge did not inhibit the reaction in regards to treatment of the organic compounds; however, it did create a high pH product stream (due to sodium hydroxide formation) that was still hazardous due to the characteristic of corrosivity. An extra neutralization treatment step was necessary to remove the corrosive characteristic from this product stream. Unfortunately, this neutralization step added a large amount of water to the process that remained in the system as a byproduct. Furthermore, upon analysis this water contained hazardous components (acetone) above regulatory levels and was thereby considered a secondary hazardous waste stream.

This secondary waste stream became hazardous through the transfer (leaching) of hazardous components. This secondary hazardous product stream was generated entirely within the post-treatment neutralization process and could have been avoided if the characteristics of the original waste were known beforehand. Pre-treatment of the waste could have been performed or a different neutralizing agent and/or process could have been used to reduce the amount of water generated through the process.

Although analyses show that the concentration of lead was reduced below regulatory levels in both the solid and liquid end products, it is uncertain where it has gone. It is assumed that much of the lead within the original waste adhered to the solid fines in the water or solubilized in the water. However, analysis of the water disproves this assumption since the lead content was so small within this medium. A possibility is that the lead was transferred into the liquid phase and then diluted to a lower concentration due to the large amounts of water added to the process.

As expected, first-order kinetic reactions had preference over second-order kinetic reactions. The treatment of all of the target analytes required first-order kinetic reactions and the amount of reagent (sodium) utilized was calculated prior to treatment so as to decontaminate only these compounds. Compounds that follow second-order kinetic reactions such as acetone and carboxylic acids were not treated through this process. These compounds could have been treated with the addition of extra sodium at the front end of the process (SET generation step).

As predicted, the treatment process converted all of the short chain hydrocarbons and carboxylic acids present in the pre-treatment sample into longer chain hydrocarbons and carboxylic acids.

The mixed waste sludge provided a challenging waste stream for the Commodore SET process because of its high moisture content. However, all RCRA organics were converted into longer chain non-halogenated hydrocarbons that are not considered hazardous. The high moisture content greatly reduced the throughput of the system resulting in treatment of only 60.8 pounds of waste.

Further studies may need to examine the following items:

- Determine optimized parameters (such as throughput, reagent amounts, etc.) for treatment of unusual mixed wastes and an operating procedure to establish optimized parameters for future waste streams.
- Examine different neutralization techniques to minimize the amount of water generated through this process.
- Conduct a metals analysis on the waste stream prior to the neutralization step to determine the fate of the contaminant.

REFERENCES

1. Code of Federal Regulations, Title 40, Protection of Environment, Part 268, Land Disposal Restrictions

2. Birch, A.J., *Quart. Rev. (London)* 4, 69 (1950)

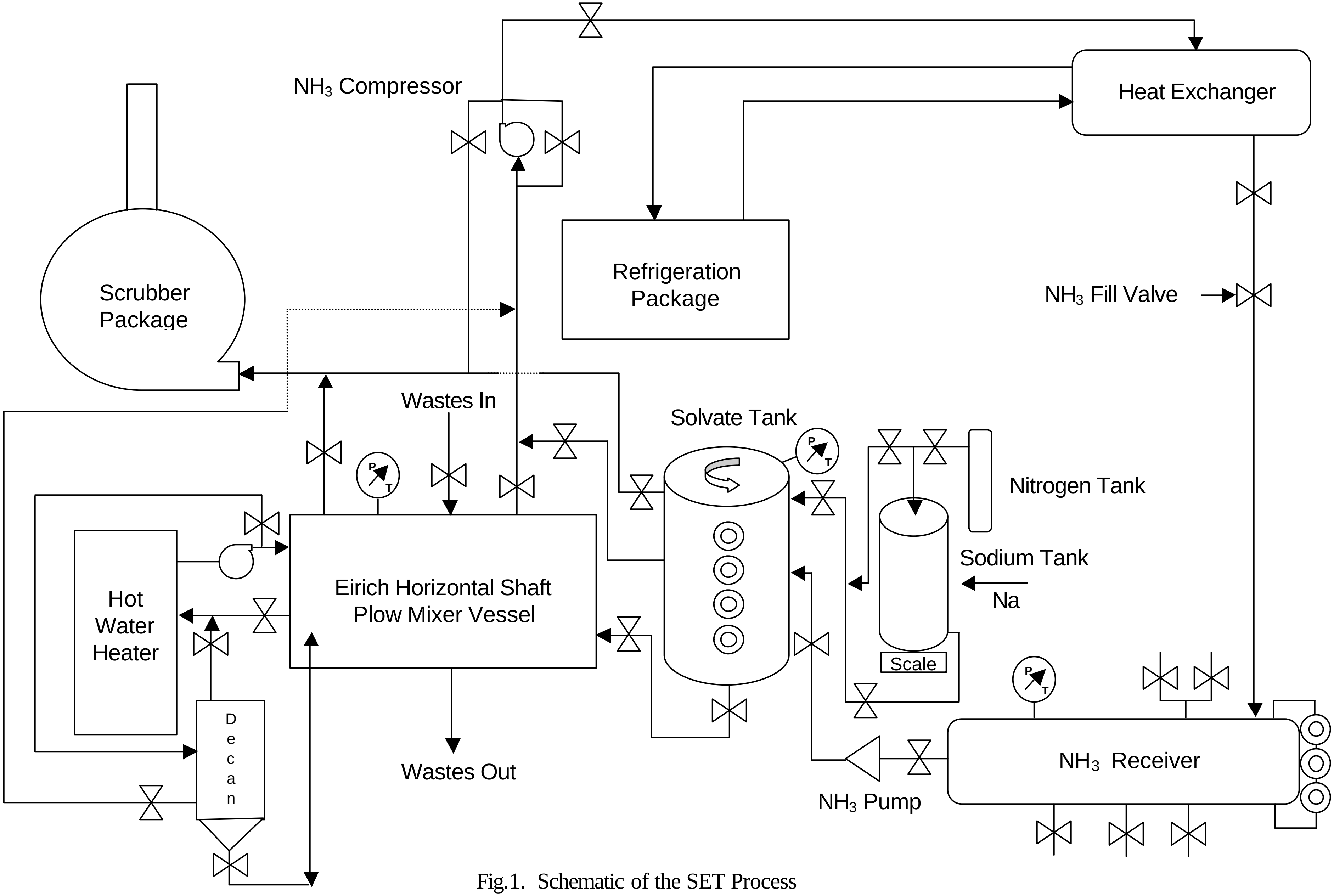

Fig.1. Schematic of the SET Process