# TECHNOLOGY CONCEPT EVALUATION

## TOXIPLEX Process for Destruction of Chemical Agents

### 1. Technology Overview

The TOXIPLEX Process, developed by Dynecology of Harrison, NY, is proposed for destruction of chemical agents [1]. The process is not designed for high salt aqueous feeds and therefore would not be appropriate for the destruction of hydrolysate or neutralents [11]. The process employs a slagging, fixed bed gasifier (British Gas/Lurgi) to destroy organic compounds at 3000°F (1650°C) and requires a treatment system to clean the product gas containing particulate aerosols and gaseous contaminants. The off-gas cleanup system generates a waste that will require disposal. The cleaned product gas consists primarily of hydrogen and carbon monoxide and can be used as a fuel for commercial boilers or for advanced gas turbines. The residual solid waste leaving the bottom of the gasifier is a slag that is converted into a vitreous frit.

The gasifier used in the TOXIPLEX process may be considered a “boiler”; however, from a regulatory perspective it may also be considered an “industrial furnace”. It is not considered an “Incinerator” based on the definition of “Incinerator” in 40CFR260.1. This technology was originally developed for producing fuel gas.

The information available for this review was evaluated relative to the application of the TOXIPLEX concept to the destruction of chemical agents. Site specific information required to assess implementation, such as requirements for systems interface, construction, permitting, schedule, demonstration and testing, etc., was not available in the information reviewed. This evaluation incorporates the comments on this process in the letter from J. Bacon (PMCD) to H. Schulz (Dynecology), dated December 22, 1997 [8].

### 2. Process Description

As shown in Figure 1 [1], the Lurgi gasifier is a cylindrical vessel in which carbonaceous material (coke) and limestone (as a fluxing agent) are fed through the top of the gasifier. A slag is removed from the bottom as a vitrified frit by quenching the slag with water. The organic feed (e.g., chemical agent) is introduced into a partial oxidation zone near the bottom of the gasifier through the oxygen and steam inlet tuyere. (The liquid form of the agent fits well with the feed requirements of the gasifier and no further preparation is considered necessary.) The product gas, which is partially oxidized, consists predominately of CO, $H_2$, $CH_4$, $CO_2$ and compounds such as $H_2S$, HCl, and others, depending on the elemental composition of the feed.

The organic feed is in contact with the partial oxidation zone for 50-100 milliseconds in the lower region of the gasifier. The temperature of the partial oxidation zone is controlled at 3000°F by regulating the oxygen to steam ratio to balance the exothermic partial oxidation of carbon with the endothermic water gas reaction. Upon leaving the partial oxidation zone, the reaction products then come in contact with an incandescent bed of coke (for one or more seconds) in the upper region of the gasifier (a highly reducing environment) where complete pyrolysis is achieved.

The product gas exiting the top of the gasifier is scrubbed free of contaminants such as $H_2S$, $NH_3$, and HCl. The product gas is a medium BTU fuel gas (300 BTU/$ft^3$), which can be substituted for natural gas in commercial boilers or as fuel for the advanced gas turbines of an integrated gasification, combined cycle power plant. All feed material that is not gasified is continuously withdrawn from the base of the gasifier as a molten slag. The slag is then fritted by quenching in water.

Figure 2 [1] provides a process flow schematic of the gasifier and gaseous effluent cleaning system. A mass balance is shown in Figure 3 [1] (based on a chemical agent feed of 11 tons per day). The mass balance of solid waste exiting from the gasifier is primarily dependent on the ash characteristics of the carbonaceous fuel used rather than the agent or toxic material destroyed. Dynecology has stated that in order to substantially reduce the solid waste exiting the gasifier and virtually eliminate any concerns related to heavy metals in the mass balance, refractory oxide packing may be used instead of coke to provide surface area for reaction. In this case, supplemental fuel will be required to ensure the desired reaction conditions are attained. The process produces a medium BTU product gas that provides a readily available source for this supplemental fuel [11].

## 3. Process Efficacy

### 3.1 Maturity of Technology

Gasification has been in commercial operation for many years. Lurgi has over 170 Gasification plants in operation including various downstream processes for gas clean-up, sulfur recovery and waste water treatment. These gasification reactors are of dry bottom design, meaning that the slag is removed in dry form in contrast to the slagging gasifier where melted slag is quenched with water to make a non-leachable frit for disposal purposes. British Gas and Lurgi developed a slagging gasifier design that was built and operated in Westfield, Scotland to produce synthesis gas [9]. British Gas discontinued its gasification efforts after natural gas was found in the North Sea.

The basic gasifier and auxiliary equipment are readily available, although they would have to be designed for site specific CWM application and integration with the plant site.

### 3.2 Process Monitoring and Control

The controlling parameter in operating the slagging gasifier to destroy chemical agents is the ratio of agent to oxygen/steam mixture. In general, adjusting the quantities of oxygen and steam flow entering the reaction zone can control the bed temperature and product gas composition.

The oxygen/steam ratio balances the exothermic partial combustion reaction, $C + 1/2\ O_2 \rightarrow CO$, with the endothermic water gas reaction, $C + H_2O \rightarrow H_2 + CO$. Variations in the ratio of hydrogen/carbon monoxide and the carbon monoxide/carbon dioxide in the gas indicate departures from steady-state conditions.

Use of the gasification process for destruction of chemical agents would not appear to significantly alter the number of process controls required, as the mass of agent added compared to the mass of coke or coal utilized for oxidation is small.

If refractory oxide packing were used instead of carbon pellets, to provide surface area for reaction, supplemental fuel would be required to ensure the desired reaction reduction conditions would be present.

### 3.3 Process Robustness

Given the large thermal mass contained within the reactor system, periodic process feed perturbations will not significantly affect the high reaction temperature, and hence reaction kinetics.

Variation in agent feed flow rate would require small adjustment in oxygen, steam and supplemental fuel flow to maintain bed temperature. The thermal inertia of the gasifier (due to the large mass of bed material) should allow small variations in feed without compromising destruction efficiency. Upon shutdown of agent feed, Dynecology reports that the gasifier can be turned down to 10 percent of its feed rate for coke, oxygen, and steam to put the unit on standby and remain in stable operation [1].

Specific data on operational reliability was not available in the information reviewed but the TOXIPLEX process would most likely achieve high operability and reliability given the maturity of the technology and the long operating history of commercially sized plants.

### 3.4 Destruction Efficiency

Dynecology reports destruction efficiencies of 6 and 7 nines when treating hexachlorobenzene and PCB's [6]. Dioxins and furans measured in the PCB tests were below 0.03 $ng/m^{3,}$ which is below the 1 $ng/m^3$ EPA limit. Destruction efficiencies for chemical agents were not available and, while required as a condition for further process development, would not be expected to be significantly different. Dynecology reports that the time required for the destructive processes to occur is less than 500 milliseconds and most likely in the range of 50 to 100 milliseconds [1].

## 4. Process Safety

Due to the rapid destructive rate (low contact time required), the inventory of toxic materials available for release from the gasifier during an abnormal or accidental release condition is low.

The low inventory minimizes both the on-site and off-site consequences for reaction vessel failure or leakage.

The high temperatures involved, the use of pure oxygen in the process, and the presence of hydrogen and carbon monoxide gas would require the use of normal industrial process safety measures. Experience with commercial operating facilities indicates that there have been no known accidents due to the release of hydrogen or carbon monoxide [2].

Dynecology recommends operation of the gasifier under a relatively low pressure (compared to commercial gasifiers) of 100 psig. A jacketed design with an inert gas is used for leakage detection and control. An even lower operating pressure could be used with a corresponding increase in vessel and equipment size and cost, if justified by a HAZOP analysis for reducing risk of failure.

For organic feed streams containing oxidizing agents such as dissolved munitions or explosives, the usual industrial safety design and operating requirements for this type of feed would need to be implemented.

## 5. Environmental Impact

The overall mass balance provided in Figure 3 identifies the quantity of waste generated. Assuming 10,000 pounds per day of VX as the agent treated, 27,293 pounds per day of solid waste would be sent to disposal. This includes 16,363 pounds per day of slag from the gasifier bottoms and 10,900 pounds per day of calcium sulfate from the gas clean-up units. The mass of slag generated is directly related to the ash content of the carbon/coal used in the gasifier. The total solid waste would be expected to be higher for treatment of the chemical agent hydrolysates, due to higher salt and water content, than for the treatment of chemical agents.

The solid waste volume from slag can be substantially reduced by substituting a refractory metal oxide (such as zirconia) to serve as the incandescent contact surface or by using a coke product with a low ash content [10]. The use of refractory packings as a bed may not be appropriate for feeds containing phosphorus due to the production of phosgene gas. A moving bed reactor design may be required an/or an external off-gas treatment process may be needed for the phosgene formed in the highly reducing environment of the reactor.

The glassy frit produced by quenching the molten slag is non-leachable and may be sold as an aggregate for road building or landfill. The practicality of utilizing solid waste products from an agent destruction plant is unlikely. Waste disposal alternatives to using the molten slag as an aggregate must be planned.

The gaseous effluent is characterized as a fuel gas with a heating value of 300 BTU/ft.[3] This gas may be used as a supplemental fuel in a turbine to generate electric power or in a boiler to generate steam. Both alternatives would require use of a flare during unit downtime. Compressed storage of the gas is possible but would be very expensive due to the cost of the storage vessels. Economic liquefaction of the gas is not feasible since the major gas components are hydrogen and carbon monoxide, which have boiling points substantially below that of natural gas.

If the gasifier were not operating, an alternative source of gaseous fuel would be required to support on-site processes. The relatively short duration of the overall program and potential non-continuous operation of supporting facilities with the TOXIPLEX process complicate the use of the product gas for off-site applications. The cost of a turbine/generator may not be economical given the short mission time. Because sulfur, phosphorus, and halogens are potentially present in an agent feed (agent dependent), off-gas treatment for the removal of these inorganic components would be required as part of the off-gas treatment process.

Since agent from ton containers will contain heavy metals, their ultimate fate when introduced into the gasifier must be determined. It had been expected that metals or ungasified components of neat agent fed to reactor, or processed agents, limestone or carbonaceous feed would be concentrated in the slag. However, tests performed at Columbia University [6] with toxic heavy metal compounds indicate the opposite: "A preponderant fraction of the metal and metal oxides introduced with the 1:2 coal/RDF pellets was carried over with the gaseous products; part was plated out on the upper, cooler portion of the refractory gasifier lining; part was trapped out with the condensed coal tars; and a negligible fraction was present in the fritted vitreous, silico-alumina slag." These results indicate the importance of determining the final dispensation solids contained within the organic feedstock, whether it be neat or treated agent such as hydrolysate.

For feedstocks containing primarily organic materials, the highly reducing environment of the gasifier precludes the formation of furans and dioxins as would be found in an incinerator during periods of operational upsets. This, coupled with the high destruction efficiency found for tested organics and the low potential inventory of the gasifier, makes the gasifier a suitable treatment for chemical warfare agent if the issues of product gas volume and mass of solid waste is acceptable. The gasifier, as a chemical warfare agent treatment option, appears to be potentially viable compared with existing process options used or contemplated today for new facilities.

### 5.1 Permitting History

There is extensive permitting history of the process for use as a gasifier. However, use of the process for destruction of hazardous materials only includes permitting as research and demonstration facilities.

## 6. Schedule

Prior to full-scale implementation a pilot scale facility would need to be built and tested, first with surrogate feed and then with agent. Dynecology expects this to take at least 3 to 6 months. The schedule for implementation of a full-scale design would be heavily dependent on permitting requirements, which are expected to be less than those required for permitting an incinerator.

## 7. Cost

Capital cost estimates were not contained within the information reviewed from Dynecology. For a 22,000 pound per day agent destruction facility, Dynecology reports a cost for operation of $1500 to 2000 per ton or about $7,500 to $10,00 per 10,000 pounds of chemical agents destroyed [1]. Supporting information was not provided.

A detailed cost analysis comparing a facility using the TOXIPLEX technology versus existing technologies, such as incinerators was not provided within the material reviewed. Adjustment values for potential improved process control, lower inventory-at-risk, and higher destruction efficiency have not been determined and are required in order to assess the magnitude of potential benefits achieved by using this technology.

## 8. Implementation at Existing Chemical Demilitarization Incineration Facilities

Dynecology proposed [1] that TOXIPLEX replace the liquid agent incinerator at the existing Tooele, Utah site, but did not provide any site specific implementation information including interface requirements for existing systems, demonstration and test plans, construction schedules, waste handling, permitting requirements and schedules, etc.

The Tooele site includes four incinerator systems, each with a specific function of treating metal parts, explosives and propellants, liquid agent or dunnage. The TOXIPLEX system is applicable to only treating liquid agent and would only replace the existing liquid agent incinerator. The other incinerator systems would still remain in operation.

For an existing agent treatment facility utilizing incineration, cost factors such as providing new interfacing or support utilities such as material handing of coke pellets, off-gas treatment, and effluent flaring would additionally have to be addressed. Although no analysis has been performed, it would appear unlikely that a cost-benefit approach could be used to justify a process change utilizing this technology.

The hazards analysis [7] for the Tooele liquid incinerator system indicates that if failures were to occur, the agent feed piping system failures are most likely. Appropriate control design, however, could be employed to limit the release of agent from a feed line failure. Since the dominant failure modes and risks do not involve failure of the incinerator system, replacement of the incinerator with the TOXIPLEX system would not be expected to lead to an overall improvement in public safety.

## 9. Conclusions

- The TOXIPLEX technology offers the potential for high agent destruction efficiency. Destruction efficiencies of 6 and 7 nines were achieved when treating hexachlorabenzene and PCBs and destruction efficiencies for chemical agents would be expected to be as good.

- The solid waste (slag) quantity produced requires disposal, since use of the waste for other purposes is unlikely. However, since the solid waste produced is a function of the ash content of the fuel, it can be virtually eliminated by using a low ash petroleum coke or a refractory metal oxide such as zirconia instead of ordinary coke as the incandescent contact surface.

- Use of the product as a fuel needs to be identified, otherwise it would have to be flared. Alternatively, it could be used as a supplemental fuel in the event that (in order to substantially reduce the production of solid waste or slag) a refractory metal oxide is substituted for coke as the incandescent contact surface.

- The thermal inertia of the gasifier would allow variations in feeds without compromising destruction efficiency.

- The TOXIPLEX process would most likely achieve high operability and reliability given the maturity of the technology and the long operating history of commercial-size slagging gasifier plants.

- Due to the rapid destruction rate (50 to 100 milliseconds), the inventory of toxic materials available for release from the gasifier during an abnormal or accidental release condition is extremely low. The low inventory minimizes both the on-site and off-site consequences for reaction vessel failure or leakage. The safety of existing support systems at Tooele may limit the safety benefits of the TOXIPLEX process. Therefore, the overall benefit for replacement of the agent incinerator at Tooele, with the TOXIPLEX process, appears to be marginal.

- For new facilities treating chemical warfare agents, this technology may be competitive with existing technologies and provide potential advantages in destruction capability and lower inventory-at-risk.

**References:**


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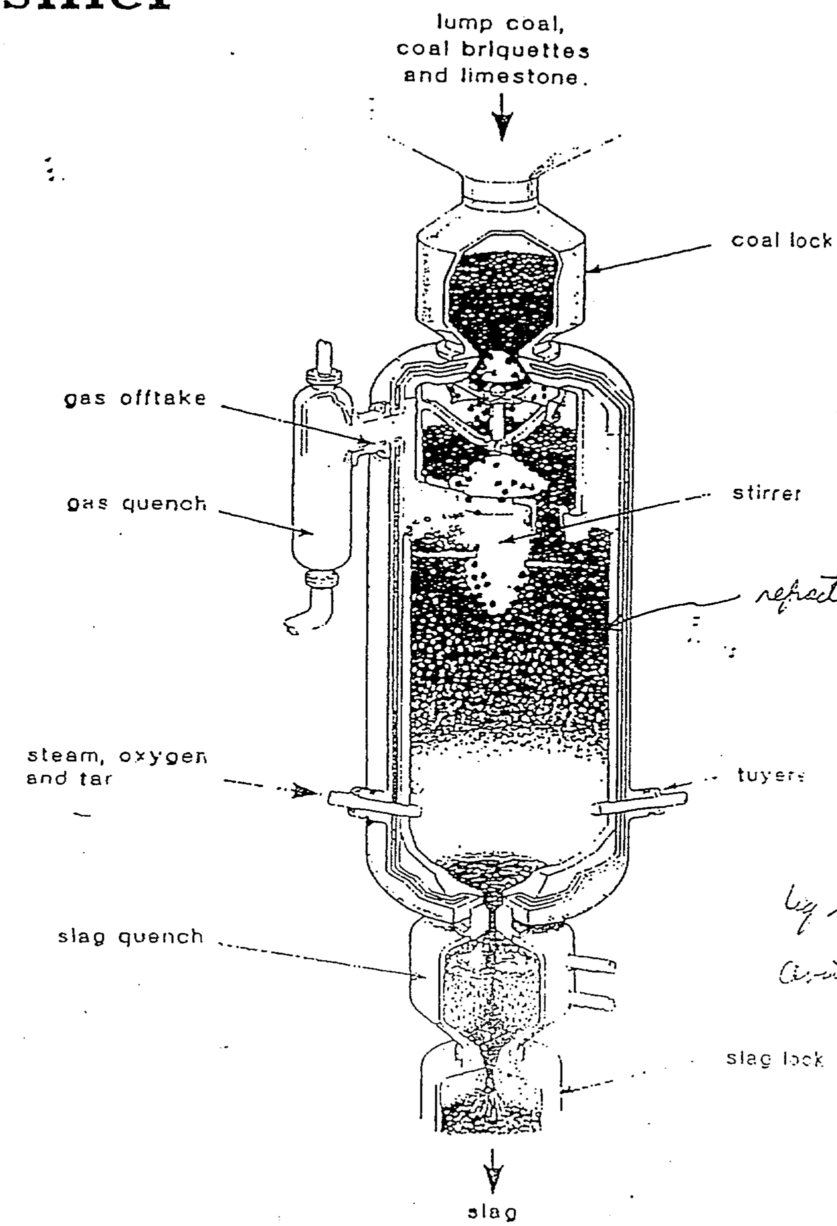
10. Fax from Helmut W. Schulz (Dynecology) to Dr. Cardito (SWEC), October 3, 1997, Re: Comments on Technology Evaluation.

11. Fax from Helmut W. Schulz (Dynecology) to Dr. Cardito (SWEC), May 18, 1999, Re: Comments on Technology Evaluation.

LURGI

# The British Gas / Lurgi Gasifier




refractory

3000 °F
400 psi

liq slag drops into water

Avoid until performance guarantee

Figure 1

35

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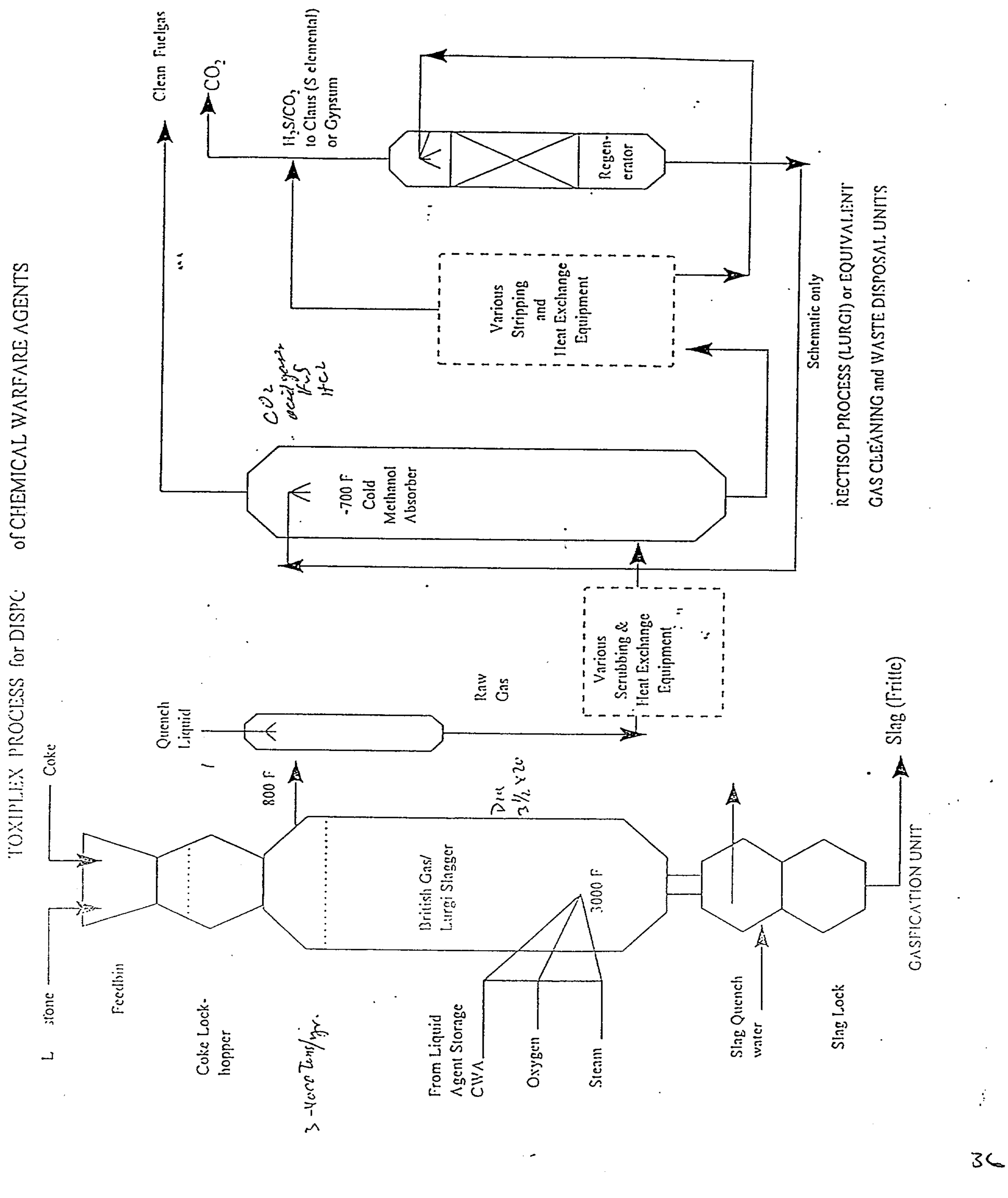


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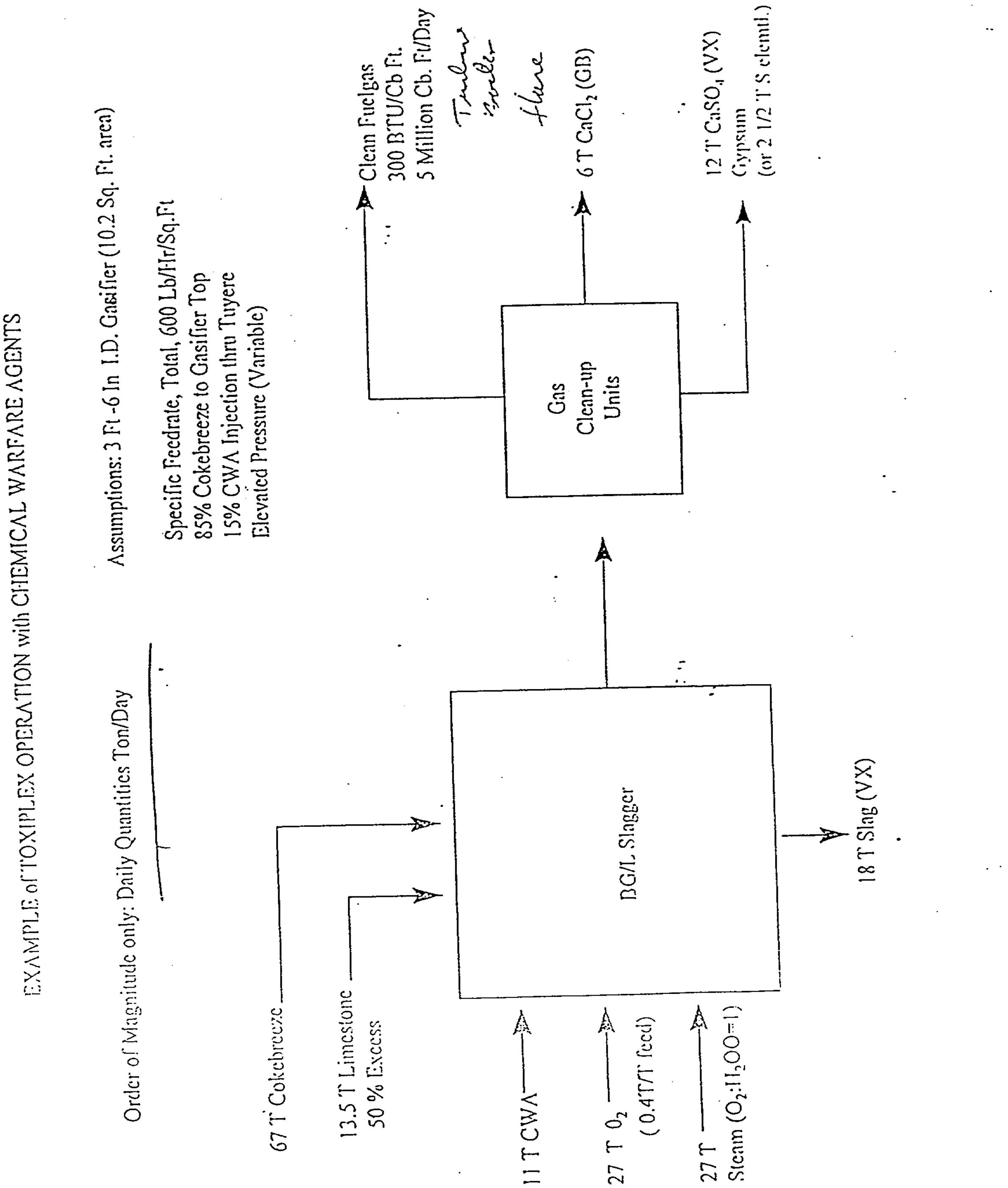


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