

## CHEMICAL CLEANING AND DECONTAMINATION OF REFINERY AND PETROCHEMICAL DISTILLATION EQUIPMENT

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### 1. Abstract

In refineries and petrochemical plants the equipment needs to be checked during planned shutdown. This can require several weeks of downtime, if columns, vessels, heat exchangers and tanks have to be drained to remove deposits and harmful gases such as hydrogen sulfide, benzene and other volatile hydrocarbons.

Formation of iron sulfide is very common in oil refineries and ethylene plants. It easily accumulates in pipes, trays, structured packings, heat exchangers or vessels. Iron sulfide deposits must be removed or kept wet before inspection of the equipment. Otherwise there is a high potential for spontaneous ignition in the presence of oxygen due to the pyrophoric iron nature. Persons in charge try to minimize exposure of workers to any situation where pyrophorically induced fires or health risks could be initiated. This paper describes chemical cleaning technologies which provide significant reduction in the downtime of the distillation equipment with elimination of a potential risk of pyrophorically induced fires and harmful gases. It also gives an overview of advanced analytical and monitoring techniques.

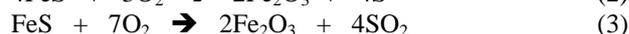
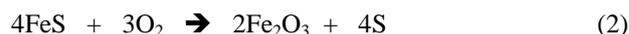
### 2. Introduction

The shutdown of a refinery or petrochemical plant is a very labour-intensive time, which requires a perfect scheduling and organisation.<sup>1</sup> Every delay means high production losses, which are rarely compensated on a later occasion. During the shutdown period often hundreds of workers are on site for mechanical cleaning, repair or replacement of equipment parts. There is a particular duty of care necessary to protect the health of the workers. Special precautions are necessary in order to avert or remove the threat of hazardous substances. There are always health hazards possible, when vessels, tanks or distillation columns are only steamed or flushed with nitrogen. Toxic hydrogen sulfide, volatile hydrocarbons or carcinogenic benzene can be released.

Iron sulfide is one of the most common fouling materials in oil refineries. Due to the pyrophoric nature of iron sulfide it can become a serious problem. The iron sulfide oxidizes exothermally when in contact with air. Most pyrophoric iron fires occur during shutdowns, when vessels, columns and heat exchangers are opened for maintenance and inspection.

Iron sulfide is formed by conversion of iron oxide (Fe<sub>2</sub>O<sub>3</sub>; rust) in an oxygen-free atmosphere in the presence of hydrogen sulfide (H<sub>2</sub>S).

Basic chemical reactions are:



The reaction of (2) and (3) is a rapid exothermic oxidation process and will ignite in the presence of combustible hydrocarbons, which are already there. FeS is also formed as primary corrosion product between Iron and H<sub>2</sub>S or as a

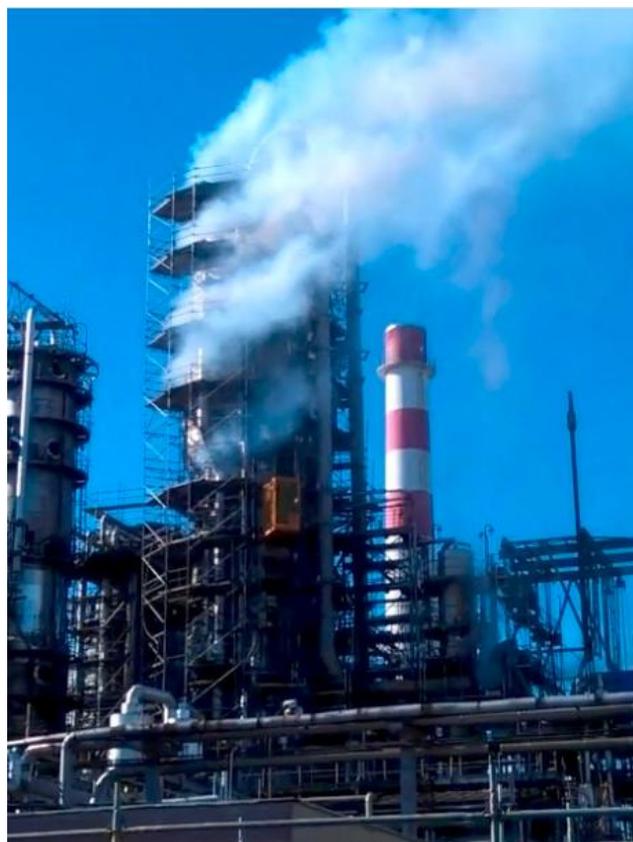


Fig. 1: Pyrophoric iron fire in a distillation column

secondary corrosion product from soluble  $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$  and hydrogen sulfide species:



The term “iron sulfide” covers a range of crystallographic forms with pyrite, troilite, pyrrhotite, mackinawite and marcasite.<sup>1</sup>

Figure 1 shows a distillation column equipped with several packing sections, where the man holes were opened for maintenance and inspection. A spontaneous ignition happened, which caused a pyrophoric iron fire. It was stopped by adding steam. The white smoke is a result of steam and  $\text{SO}_2$  gases.

### 3. Cleaning and decontamination technologies

Chemical cleaning technologies are required when refinery equipment such as distillation columns, vessels, pipes and heat exchangers must be cleaned in a single processing step<sup>1,2</sup>. In most cases the chemical cleaning procedure includes a safe removal of hazardous gases and should be finished at the latest after 8 - 16 hours. Conventional cleaning procedures like acid cleaning, chelating solutions or strong oxidizing chemicals (i.e.  $\text{KMnO}_4$ ,  $\text{NaClO}$ ,  $\text{H}_2\text{O}_2$ ) are not suitable when pyrophoric iron sulfide, hydrogen sulfide, benzene and other volatile hydrocarbons have to be removed or eliminated at the same time. Many customers renounce the usage of acids or strong oxidizing chemicals to avoid corrosion attack or unwanted chemical reactions during shutdown procedures. The required decontamination goal for benzene,  $\text{H}_2\text{S}$  and Lower Explosive Limit (LEL) is zero or near zero. Cleaning and decontamination chemicals are injected into an aqueous phase. This requires the draining of the hydrocarbon phase first. Often a 0.5 to 2.0 wt% cleaning solution is circulated with a high flow rate at temperatures between 60 to 80 °C.

Figure 2 shows the common flow directions when cleaning and decontamination programs are used<sup>3</sup>. The most efficient cleaning and decontamination method is the recirculation, where the chemical program is added within a very short period of time to be circulated with the wash water for minimum 6 to 8 hours. The cleaning solution is flowing down from the top to the bottom, providing a perfect contact with the metal surface, deposits and gases. Cascading requires a continuous injection with far higher chemical amounts, when reflux of the cleaning solution is not possible. Steaming with continuous injection of a chemical program reduces the downtime by up to 75% compared to conventional steam-out methods. The steam pressure should be in the 3 to 6 bars range to avoid thermal decomposition of the chemical.

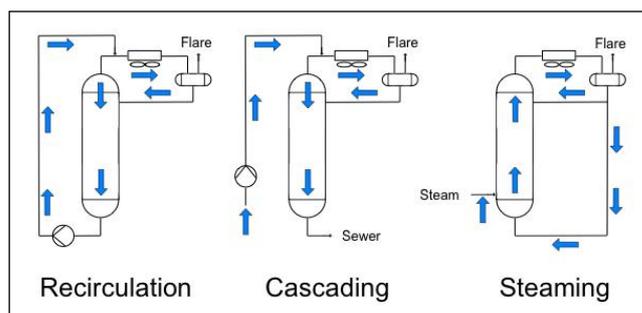


Fig. 2: Chemical cleaning flow directions

The difficulty with cleaning and decontamination procedures in a single processing step is the simultaneous treatment of solids, liquid and gases. Sticky deposits have to be removed from the metal surface, pyrophoric iron species must be oxidized and encapsulated dangerous gases (i.e.  $\text{H}_2\text{S}$ , benzene) and associated odours have to be eliminated in a safe manner. Distillation columns equipped with fouled packings (figure 3) bear the risk of channeling effects during cleaning operation. Clogged heat exchanger tubes minimise the cleaning performance, when flow through these tubes is virtually impossible.

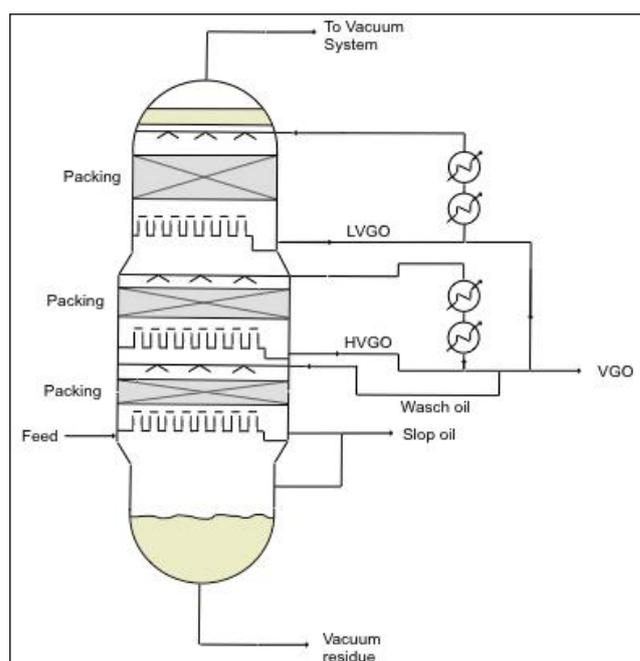


Fig. 3: Vacuum distillation column with packings

### 4. Environmentally friendly cleaning procedures

In most cases wash water is used and additional solvents are not required other than to bring down the unit as part of the normal cooling process prior to the decontamination process. The chemical constituents should be biodegradable and compatible with all metals. The disposal and/or treatment of waste after cleaning and decontamination is always a consideration.

Kurita provides a wide range of various products such as cleaning chemicals, decontamination agents or combinations thereof. All product solutions are high quality programs, adapted to specific customer requirements. A unique combination of mild surfactants gives excellent service for numerous types of cleaning and decontamination. The formulation contains an alkyl-dimethyl amine oxide that supplies oxygen to FeS in a rather slow and impeded manner (compared to many other oxidizers). This allows to oxidize pyrophoric iron during the application without creating the dangerous exothermic problems of common oxidizers such as hydrogen peroxide, potassium permanganate, and bleach. In addition it works as an oxidizer in both liquid and vapor phase applications—as long as the deposit is saturated with the cleaning solution.

The chemistry is non-toxic, non-hazardous and completely biodegradable, contains no volatile hydrocarbons, and has no flammability concerns. This eliminates the storage and handling concerns frequently associated with chemicals used in refineries. The surfactants are highly sensitive to sulfides and provide for a mild oxidation of any hydrogen sulfide and pyrophoric iron sulfide that might be present. Hydrogen sulfide and pyrophoric iron species are eliminated, not simply ‘chemically bound’ with other material only to be released elsewhere when the pH or temperature changes.

With use of mild surfactants the benzene is extracted much faster into the water. The benzene evolves from the water at normal or faster rates than would be expected of untreated water. The major effect is that benzene can be removed from the walls and sludge in process equipment without additional mechanical action. When steam or a carrier gas (i.e. nitrogen) is put through the high-benzene wash water, the volatile benzene can be diverted to the flare or other collection systems. The decontamination process does not hamper the ability of benzene to be stripped from water. During the chemical cleaning and decontamination the low explosion level (LEL) compounds are released from the process equipment and sent to flare with the result of zero or close to zero concentrations.

The 0.5 to 2 wt% aqueous solution of alkyl-dimethyl amine oxide based surfactants provides a measurable and controllable temporary emulsion. Hydrocarbon liquids and vapours are emulsified. Agitation and circulation will keep the aqueous cleaning solution in a temporary emulsion phase. A clean oil/water separation is achieved after the decontamination process is completed. Without agitation and circulation separation typically occurs within 3 hours without additional chemicals. This allows for easier (and often less expensive) disposal or treatment of the waste materials left over after the decontamination. A major benefit to the customer is that very low COD wastewater can be obtained without additional costly tankage or post-job treatment.

## 5. Treatment planning and monitoring

The chemical cleaning and decontamination is the practical result of a proper prearrangement with many technical discussions, risk analysis, preparatory work and definition of the key performance indicators.

Ideally, deposit samples are available from the relevant system at an early stage to allow analysis and proper selection of cleaning chemicals as well as definition of a cleaning strategy<sup>2</sup>. Deposits found in refinery water and process systems may vary widely in composition depending on the parent system and operating parameters. Fig. 4 shows a selection of deposits found in various systems and their diverse appearance.



Fig. 4: Deposits found in various systems

Deposit analyses should follow a well defined standard procedure delivering the most relevant information in a reasonable time frame at acceptable cost. A typical procedure comprises the following steps:

- Sample drying to remove water or volatile organics
- Ignition loss at 550 °C
- Ignition loss at 800 °C
- X-Ray fluorescence analysis of residue (XRF)

Deposit compositions should always be reported based on dry matter. The ignition loss at 550 °C will give an indication of organic content, the ignition loss at 800 °C (exactly: the difference between 800 °C and 550 °C) an indication of carbonates, frequently found in process water systems. XRF of the residue will quantify the elemental composition of elements like Na and heavier (inorganic composition).<sup>2</sup>

During vessel passivation and removal of deposits iron and other sulfides may convert from a pyrophoric state to a non pyrophoric state, especially in mixed deposits. Therefore, deposit samples taken for analysis may still contain sulfur in various sulfide forms. This non pyrophoric reduced sulfur species will be oxidized during the first stage of ignition loss analysis and sulfur will be lost as SO<sub>x</sub> gas, which will

incorrectly indicate a high organic content and falsify the mass balance. For correct quantification of S in refinery and petrochemical deposits, sulfur should be measured in the dried sample using elemental analysis.

Deposit samples containing a high proportion of organic material (typically > 50 wt%) can additionally be analyzed via spectroscopic techniques (IR and NMR spectroscopy) which allows a characterisation of the organic content.

Merging the results of all analyses, the detailed composition of the deposit becomes available, which helps a lot in selecting the correct cleaning chemical and strategy. If not enough time is available for the detailed analysis prior to performing the cleaning job, the analysis will still be useful since it will give information about deposits to be expected in the future and possibly in similar plants as well.<sup>2</sup>

During cleaning and decontamination liquid samples can be taken on an hourly base to monitor the progress of this procedure. Each cleaning and decontamination is an individual process, which needs a clear definition of the monitoring tools and parameters in accordance with all stakeholders.

Typical monitoring parameters are:

- Appearance of the samples
  - o colour and turbidity
  - o colour intensity
  - o sediment
- Emulsion strength (visible test)
- Concentration of the cleaning solution
- pH value and conductivity
- Temperature conditions
- Iron concentrations
- Sulfide concentrations
- VOC concentrations
- Benzene concentrations
- H<sub>2</sub>S concentrations
- LEL compounds
- etc.

An indicator for a completed decontamination operation are the low concentrations of hazardous gases measured in the gas phase. (figure 5 and table 1) at the end of the decontamination.

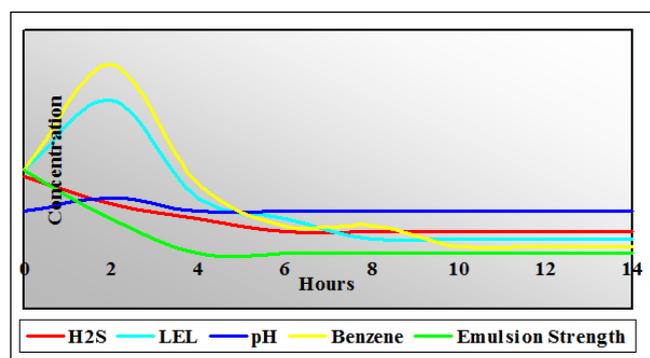


Fig. 5: Cleaning and decontamination of a vessel

Time	Temperature cleaning solution [°C]	Concentration cleaning solution [%]	VOC [ppm]	Benzene [ppm]	H <sub>2</sub> S [ppm]
13:00	60	2	-	-	-
14:00	60	2	21	12	10
15:00	60	2	24	15	6
16:00	60	2	25	15	3
17:00	60	2	15	3	2
18:00	60	2	10	2	1
19:00	60	2	9	1	1
20:00	60	2	8	1	1
21:00	60	2	7	0	0

Tab. 1: Decontamination of a distillation column

The concentrations were defined as key performance parameters before starting the cleaning job.

## 6. Case study: Photometer use as advanced monitoring tool

Photometers are well known for water side analyses, but they can also be a useful tool for process side cleaning operations, especially if heavy organic deposits are to be cleaned. These deposits color the cleaning solution so intensely that a visual evaluation of the cleaning solution loading becomes impossible. Although water based cleanings are always preferable from safety, environmental and cost point of view, some deposit types containing heavy organic (tar like) substances require solvent based cleaning operations. This case study describes the use of a photometric technique for monitoring a solvent based cleaning, but the methodology can also be transferred to water based cleanings.

In a major European refinery, a significant deterioration of heat transfer was observed in the hot preheat train of a crude unit, especially in 2 heat exchangers at the end of the train. A deposit sample comprised about 40 wt% of organic components, 30 % corrosion products and 10 % silicates.



Fig. 6: Fouled heat exchanger (CDU preheat train)

The organic part was identified using IR spectroscopy as heavy aliphatic hydrocarbons. The affected heat exchangers had served Russian export blend (REB) type crude on the tube side (heating from 220 to 250 °C) and vacuum residue on the shell side (cooling from 360 to 240 °C). Based on the process configuration, a relatively strong fouling was assumed on the shell side, while the expected fouling on the tube side was less severe. The cleaning equipment comprised the following components:

- Cleaning truck with strong pump (20 m<sup>3</sup>/h recirculation rate)
- 1 m<sup>3</sup> plastic intermediate bulk container (IBC) as buffer tank
- 4 additional intermediate bulk containers (IBC) for intermediate storage of cleaning fluid
- Steam heated heat exchanger
- Hoses and connectors
- Photometer

The chosen cleaning strategy was the recirculation method and advanced analytical monitoring of the process was done by diluting cleaning liquid samples in gas oil, measuring the extinction of the diluted samples at 600 nm (other wavelengths are also possible) and calculating the corrected extinction as follows:

$$E_c = E_m \times f \quad (6)$$

with  $E_c$  = corrected extinction

$E_m$  = measured extinction

$f$  = volumetric dilution factor

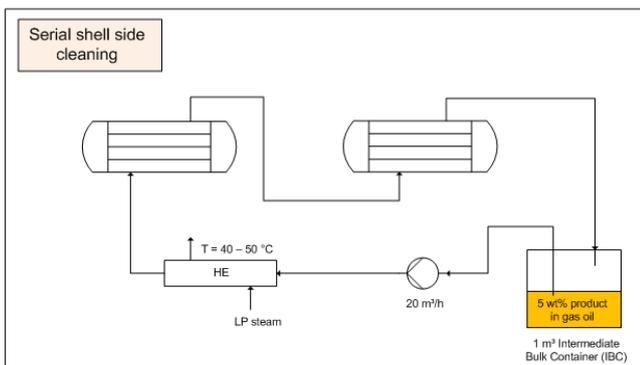


Fig. 7: Cleaning setup for heat exchangers

The exchangers were isolated from production process and emptied as much as possible. The cleaning liquid was gas oil (flash point > 80 °C) as solvent and 5 wt% of a mixture comprising a strong anionic surfactant and a dispersant. On the shell side, the exchangers were connected to the tank, the pump and the heat exchanger and the cleaning solution was circulated at about 50 °C. The total volume of cleaning liquid was about 5 m<sup>3</sup>. The cleaning progress was monitored photometrically, a quick darkening of the solution being noted. Already after 5 minutes, the solution was black, so that it had to be diluted by a factor of  $f = 50$  for the photometric measurement. After 30 minutes the cleaning

procedure had to be interrupted due to operational reasons. The cleaning liquid remained in the closed plant overnight, the procedure being resumed the next morning. The development of corrected photometric extinction is shown in Fig. 8.

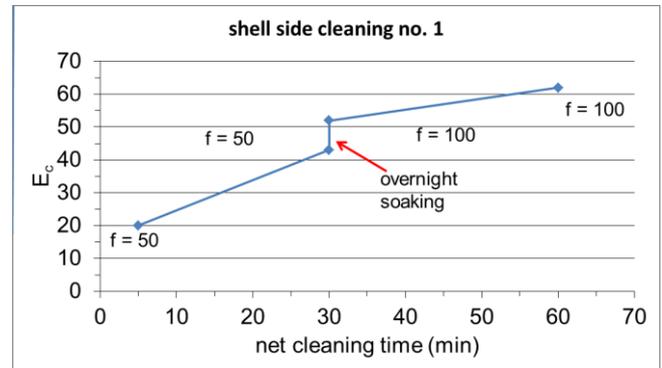


Fig. 8: First step of cleaning procedure

After soaking overnight, it was necessary to dilute the sample by a factor of  $f = 100$  in order to achieve a reasonable photometric measurement. During the following 30 minutes (temperature about 50 °C), the cleaning solution turned extremely dark, indicating high loading with foulant and dirt. A sample of cleaning solution that had been drawn the previous day showed a lot of black sludge / sediment that had settled overnight. This was another hint towards a high loading of the cleaning solution with dispersed solids. The solution was discharged to the refinery slop system, a fresh batch of solution prepared the same way and cleaning resumed. The development of corrected extinction during this second step is shown in Fig. 9.

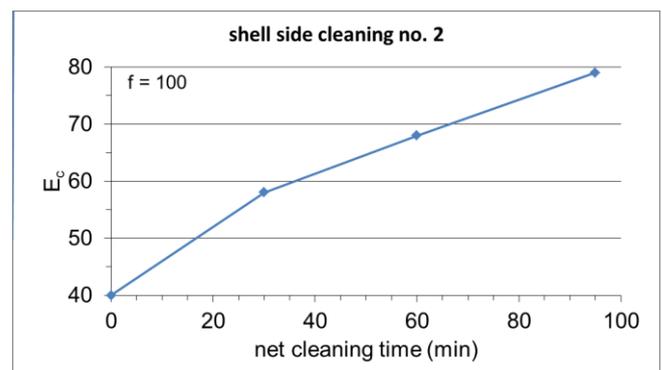


Fig. 9: Second step of cleaning procedure

After starting the second cleaning cycle, the solution again turned black very quickly, which indicated the dissolution of remaining sludge and deposits. After 90 minutes the procedure was stopped and a third batch of cleaning solution prepared. The development of corrected extinction during this third phase is shown in Fig. 10.

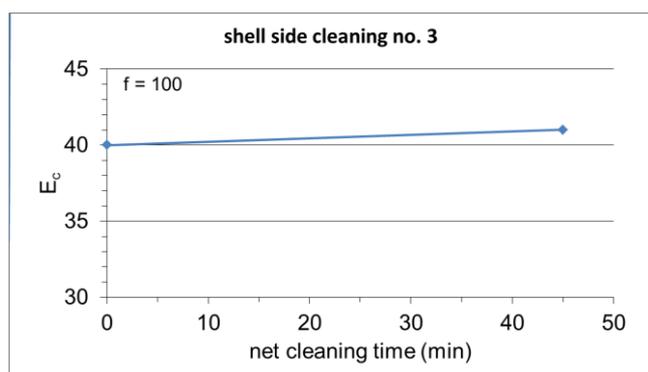


Fig. 10: Third step of cleaning procedure

After 45 minutes, no significant increase in corrected extinction was noted anymore. Thus completion of the cleaning procedure was concluded. After another 15 minutes the procedure was stopped, the cleaning fluid drained and the heat exchangers coupled to the process again. The strongly fouled shell side of the exchangers was effectively cleaned by the procedure, indicated by an increase in heat transfer by 10 %. The application of the photometric procedure allowed a more precise determination of the cleaning solution loading, helping in the decision when to exchange the solution by a fresh batch and saving overall cleaning time.

## 7. Conclusions

Cleaning refinery and petrochemical process units is a complex task that requires thorough analyses, proper selection of cleaning products and procedures as well as advanced treatment monitoring. Water based cleaning fluids should be the first choice due to environmental, safety and cost considerations, but some deposit types containing heavy organic compounds may still require organic cleaning solutions. Deposit analyses carried out prior to the cleaning job will give valuable information and guide the product selection process. Advanced analytical monitoring techniques employing simple equipment such as photometers, pH and conductivity meters help in achieving the maximum cleaning effect in the shortest possible time. Since the cleaned equipment can be taken online sooner, this provides significant cost savings. Pyrophoric iron deposits require a specialist approach for cleaning and disposal. Kurita can provide the entire range of cleaning services from initial deposit analysis and product selection to final disposal of cleaning solutions fully compliant with all local regulations.

## REFERENCES

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