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Petrochemical Waste Management

Sound environmental management includes the proper management of waste . This paper reviews the basic rules of good management practice illustrated by some examples from chlorine derivatives production and gives the main considerations governing the best available techniques for organochlorine waste thermal treatment .

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The three rules of good waste management

As a general rule, the first step of waste management is the reduction of the waste and by-products created

As an example, the manufacture of chloromethanes initially used the thermal chlorination of methane . This process obviously created, due to the use of methane as raw material , a large amount of hydrochloric acid by- product .

To reduce the HCl by product formation, a second generation of processes produces methyl chloride using methanol and HCl as raw materials. In a second step, methyl chloride is chlorinated into methylene chloride and chloroform .

Furthermore, the thermal chlorination, which selectivity is poor, has been replaced by photochlorination or radical-assisted chlorination, permitting an overall raw material efficiency above 99.5%, and reducing the organics waste formation in a ratio of 10:1 .

The second rule of waste management is the valorisation of the by-products

In the previous example, the use of methanol and hydrochloric acid in the first step, permits the recycling of part of the by-product HCl of the second step, Depending on the average degree of chlorination of the finished products, a nearly balanced process can be realized . But most of the producers of chloromethanes are also producers of vinyl chloride monomer. This important process implies a step of oxychlorination of ethylene to produce ethylene dichloride, using ethylene, air or oxygen, and HCl as raw materials .

It is therefore possible to recycle all HCl by-product including that from chloromethanes production in this process, provided the production units are on the same site and the suitable purity is obtained .

The vinyl chloride monomer process is another good example of waste management. Historically, the old process starting from acetylene and HCl was very selective, having more than 99% efficiency on raw mate-

rials . This was due to the high reactivity of the triple bond of acetylene. Unfortunately , acetylene production was less efficient and acetylene was replaced in the years 1960s, by ethylene .

Vinyl chloride manufacture uses 3 main reactions .

A direct chlorination of ethylene to produce EDC ethylene dichloride. This reaction is highly selective; a pyrolysis of EDC to produce vinyl chloride and HCL. This step is selective provided there is a limitation of the transformation of EDC to less than 50 - 60%, as well as limitations of pressure and temperature; the third reaction is the oxychlorination of ethylene, using oxygen (from air or pure oxygen) and HCL as reactants. This reaction is conducted in fluidised or fixed beds, and represents the main source of organochlorine waste from the process, although the process has been continuously improved. About 3% of the vinyl chloride production results in waste or by-products.

To valorize these wastes, the producers are using different processes:

An oxidation process using the waste as raw material, allows the recovery of at least the chlorine content as HCI, which is recycled; the TRI PER process, using the light fraction (50- 60%) of the waste as raw material, transforms the waste into trichloroethylene and perchloroethylene for sale as marketable products, or raw materials, the Tetra-Per process, also using the light fraction of the waste as raw material, transforms the waste into perchloroethylene and carbon tetrachloride.

Since the Montreal Protocol for the protection of the Ozone Stratospheric layer, no longer allows CFC 11 and 12 production, (the main use of carbon tetrachloride), and since carbon tetrachloride itself is regulated by the Montreal Protocol, the uses of this product are now very limited.

The Tetra-Per process therefore has been modified to focus the production on perchloroethylene. In summary, 50-60% of the vinyl chloride manufacture waste is recycled in marketable products.

The residual fraction, containing the most heavy parts, is thermally decomposed with recovery of hydrochloric acid, either recycled in the process itself, or as HCI commercial solution.

The third rule of waste management, after maximum reduction and recycling, is to dispose of the waste safely

The vinyl chloride process will be taken as an example for application.

Waste management in the manufacture of vinyl chloride

The European Producers of VCM and PVC under the auspices of the European Council of Vinyl Manufactures (ECVM) have conducted a two years study on how to minimize the environmental impact of the manufacture of PVC and to define best available techniques .

All scurces of impact were analysed: water, air, soil, waste. With regard to solid waste, the main sources are the heavy fractions from the 3 reactions and specially the oxychlorination step.

The total amount is = 0.03 ton per ton of VCM produced .

In some plants, the waste is subject to oxidation and transformed into CO_2, HO_2 and HCI which is recycled in the process.

As already mentioned before, other producers are using different techniques to recycle a large fraction of this waste . About 50 - 60% of the waste is transformed into marketable products or raw materials such as trichloroethylene and perchloroethylene .

The fractions and residues not directly reusable are submitted to combustion under controlled conditions into water, carbon dioxide and hydrochloric acid. In this situation hydrochloric acid can be recovered from the off-gas and can be either recycled as feed stock to the oxychlorination plant for the production of more ethylene dichloride, or recovered as hydrochloric acid solution .

Spent catalyst, metal sludges and coke from EDC cracking is another source of waste obviously, in a quantity much lower than the previous one, e.g. a few tons per year. However, this waste requires attention because traces of furane compounds, mainly hepta and octochlorodibenzofuranes, are formed in the oxychlorination reactor, using a copper catalyst. These compounds are fixed on the catalyst.

As a result, the oxychlorination process water effluent, which contains the fine catalyst losses, is subject to adequate treatment .

Dissolved copper can be removed by precipitation and filtration together with the non dissolved particles .

When present in the aqueous effluent, the furane compounds are all adsorbed in the suspended solid particles which are present. This is the result of the very high value of the Koc coefficient of such compounds (i.e. the partition coefficient between water and organic carbon).

Therefore, they can be removed from the effluent with traditional technology such as flocculation, settling, and filtration, with the addition of adsorbent material when necessary .

A third source of waste can be the biosludges from a classical aerobic biological purification of the wastewater treatment plant.

With biological treatment, and depending upon the efficiency of the upstream physico-chemical treatments of the process water, some additional removal of the furane compounds may take place by adsorption. If contaminated, this sludge must be disposed of properly.

In summary, by a combination of appropriate and multiple technologies adapted to each individual situation, the impact of both atmospheric and water emission and waste disposal are reduced beyond the most stringent requirements of health-based and environmentally based regulating prescriptions and quality objectives. This is the main purpose of sound environmental management. ■

Top Picks

Dana Petroleum Egypt Joint Venture Approved

29 November 2011- Dana Petroleum plc (Dana) announced that the Egyptian Ministry of Petroleum has approved «Petro Kareem»- a new joint venture between Dana and the Egyptian General Petroleum Corporation. Petro Kareem will produce oil and gas from the Lorcan Development lease, within the North Zeit Bay (NZB) concession, located onshore in the Gulf of Suez, 320 km south east of Cairo. The NZB Production Sharing Contract (PSC) area, in which Dana holds a 100% interest, consists of two wells currently producing oil via the Lorcan Processing Facility, Lorcan-1xST and Fin-1x, with the potential to add a further four wells (Matr-1xST, Calumn-1x, Abydos-1x and Omar-1x), pending development lease approval. Dana estimates that there are reserves of 10 - 12 million boe (100% Dana) within the PSC area with the potential of considerable upside beyond this. During the early production testing of the Lorcan lease, production of more than 0.25 million barrels of oil has already been achieved. This positive news follows several significant exploration successes for Dana Petroleum Egypt during 2011.

Elsewhere, on the onshore East Beni Suef concession (Dana 50%, Apache Operator 50%) enjoyed further exploration success later in the year, with two oil discoveries made firstly on 1 June 2011 by the WON C-1X well and secondly via Fayoum-3x on 2 October 2011. Both discoveries have been declared commercial and have had development leases awarded by the Ministry of Petroleum.

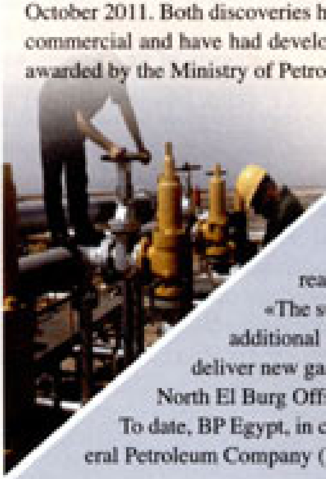
Kuwait Energy Announces Flow Rates from Abu Sennan Discoveries

Kuwait Energy

15 October, 2011 - Kuwait Energy Company KSCC "Kuwait Energy", announced that initial tests on its recent Egyptian discoveries on the GPZZ-4 and Al Ahmadi-1 wells, revealed flows of gas and condensate.

The wells are located in the Abu Sennan concession in the Egyptian Western Desert. Kuwait Energy, holds a 50% working interest in the concession. The remaining 50% is held by Beach Energy Limited with a 22% working interest and Dover Petroleum with a 28% working interest. The GPZZ-4 well was drilled first as part of a six-well drilling program in the Abu Sennan concession. Initial tests from the Lower Bahariya formation recorded a daily production flow rate of 847 bbls of condensate and seven mmscf of gas per day. The GPZZ-4 total production flow rate from the Lower Bahariya is equivalent to approximately 2,000 boepd. Additionally, in this well a combined test from the Abu Roash G and Upper Bahariya formation produced at initial rates of 151 bbls of condensate and 1.6 mmscf per day. The Al Ahmadi-1 well showed a daily production flow from the Abu Roach G of 800 bbls of condensate and 13.5 mmscf of gas, a total production flow rate equivalent to approximately 2,900 boepd. This well also tested the Lower Bahariya formation with production of 72 bbls of condensate and 1 million standard cubic feet per day.

BP Makes Gas Discovery in Egypt's Nile Delta



24 October, 2011 - BP Egypt announced the Salmon gas discovery in the North El Burg Offshore Concession, Nile Delta. Salmon is the third gas discovery BP has made in the concession following Satis-1 and Satis-3 Oligocene deep gas discoveries. Salmon, drilled by IEOC, the affiliate of ENI in Egypt, on behalf of concession operator BP, is located 50 kilometers to the north of Damietta. The wireline logs and pressure readings confirmed the presence of gas in two shallow Pleistocene intervals. The well was drilled by Scarabeo IV rig in water depths of 87m and reached a total depth of 1600m. Further appraisal work to evaluate the resources is underway. BP Egypt stated «The success of Salmon highlights the great potential of the shallow reservoirs within the Nile Delta, and helps unlock additional resources in surrounding acreage. It demonstrates the ongoing cooperation with the Ministry of Petroleum to deliver new gas discoveries and incremental supply to meet the future growth of the gas business in Egypt. The parties to the North El Burg Offshore Concession agreement are: BP (operator 50%) and IEOC (50%).

To date, BP Egypt, in collaboration with the Gulf of Suez Petroleum Company (GUPCO), BP's JV Company with the Egyptian General Petroleum Company (EGPC), has been responsible for the production of almost 40% of Egypt's entire oil production.