PERSISTENT ORGANIC POLLUTANTS AND OTHER HAZARDOUS WASTES FROM TITANIUM PROCESSING INDUSTRY - THE KERALA MINERALS AND METALS LIMITED, INDIA

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Abstract

It has been known since 1998 that the processing of titanium via chloride route generates persistent organic pollutants like dioxin, furan, poly chlorinated biphenyls etc. The inventory of toixins also includes heavy metals and polycyclic aromatic hydrocarbons, most of which are carcinogenic and mutagenic. Costly remedial measures have been implemented by the industry in Europe, North America and Japan during the last decade. Prices of titanium products more than doubled due to this. However, it has been business as usual in the Kerala Minerals and Metals Ltd, a public sector undertaking and the only producer of titanium dioxide pigment via chloride routein India. With about half a million tons of solid waste containing highly hazardous substances, which will stay in the eco-system, the biosphere and the breast milk for hundreds of years into the future, the industry is neck deep in crisis.

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Introduction

The Kerala Minerals and Metals Ltd (KMML) processes ilmenite mined from the beach sands of Kollam district using 21 other raw materials. The main products are titanium dioxide pigments, nano-titanium and titanium sponge. Ilmenite (60% TiO_2) is converted to synthetic rutile (SR) in the beneficiation plant. In the Chloride Process, SR is converted to titanium tetrachloride ($TiCl_4$) gas in a chlorinator (fluidized bed reactor) in the presence of chlorine gas at 850° C to 950° C, with petroleum coke added as a reductant. The gaseous raw product stream is purified to separate the titanium tetrachloride from other metalic chlorides by fractional condensation (Ferric chloride -$FeCl_3$), double distillation (trace metal chlorides) and chemical treatment (vanadium oxychloride -$VOCl_3$). The purified $TiCl_4$ is then oxidized to Titanium Dioxide (TiO_2) at 985° C, driving off chlorine gas, which is recycled to the chlorinator. Aluminum chloride is added in the oxidation step to promote formation of the rutile crystal, which is the TiO_2 product.[1] The main reactions are shown below:

$$2FeTiO_3 + C \rightarrow 2Fe + 2TiO_2 + CO_2 \quad (1)$$
$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2 \quad (2)$$
$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \quad (3)$$

Dioxin from Chloride process

Dioxins are produced when carbon, oxygen, hydrogen and chlorine atoms burn at temperatures above 260 C. Very small quantities of dioxin are produced by some micro-organisms, in forest fires and in volcanoes. Dioxin, furan and PCBs are persistent organic pollutants (POP), which bio-accumulate in the food chain. **The anthropogenic dioxin source came into existence with beginning of the chlorine chemistry in the modern era. Dioxins are among the most toxic substances known to us. TCDD, a dioxin congener is known to be 3500 times toxic as endosulfan. They can cause cancer, genetic mutations, untoward pregnancy outcomes, infertility, immune system dysfunction, reduction in breast milk, kidney diseases and a long list of autoimmune diseases. It is a slow killer and an aging agent.** All the world governments have agreed to ultimately eliminate all the POPs in the long run and reduce all the emission to as low as achievable. The emission the West European and the North American countries came down to almost a tenth during last two decades.

The chlorination process has all the conditions necessary for the formation of dioxins and furans: a carbon source, a chlorine source, and a heat source. The US EPA had since 1998 “catalogued many different sources of dioxins and furans, the vast majority of which involve these three critical conditions of carbon, chlorine and heat. The results of EPA’s record sampling and analysis for wastes from the production of titanium dioxide confirmed the expectation that dioxins and furans were likely to be formed during the chlorination process.” Based on to the U.S. Toxics Release Inventory, one titanium dioxide production facility was the second largest PCDD/PCDF source in the U.S. in 2000 [2] Metals like copper, iron, zinc, aluminum, chromium, and manganese are known to catalyze PCDD/PCDF formation.[3]

In 1998, the US Environmental Protection Agency (US EPA) determined that the titanium industry was a major contributor of dioxin. According to the US EPA's 2003 toxic release inventory, DuPont's three titanium plants released 56,142 grams of dioxin.[4] This was about 60% of the total national emission in the reporting year and about three times the current release from the US. The company had accepted the responsibility and claims to have brought down the emission to 10% by the end of the last decade.

<u>High Expsoure and Low Monitoring</u>

The Central Pollution Control Board (CPCB) estimated that the national emission of dioxin from India was more than the total emission by EU, USA and Canada. Similarly, the concentration of dioxin in breast milk and food (of animal origin) is the highest in India, some three times higher than that in Europe. The major exposure routes are mothers' milk, fish, meat, milk and egg. In a study report published in 2007, the Central Pollution Control Board says that we have already crossed the limits.[5] In India, there are only two government laboratories and a few scientists who have been trained to do the analysis. Even though nearly half the foods-drinks consumed in India come out from an industry, there is hardly any monitoring of toxins in fertilizers, fodders, feeds and other food related raw materials.

<u>KMML’s legacy</u>

About 210,000 tons of 22 raw materials are used every year to produce 40,000 tons of finished products by KMML. The toxic hazardous waste generated are (a) heavy metals and radioactive isotopes like thorium and uranium daughters found in the raw materials and (b) compounds generated during the chemical processing. The latter include pentachlorodibenzo para dioxin (PCDD) and furan (PCDF), hexachlorobenzene (HCB), polychlorinated biphenyl (PCB) and Polycyclic Aromatic Hydrocarbon (PAH). Besides these, intermediate products like titanium tetrachloride and nanoparticles of titanium are also highly toxic. **These valuable items also escape from the factory as the audit report of the Comptroller and Auditor General (CAG) reveals high level of wastage.[6]**

<u>US EPA on the sludge</u>

Titanium dioxide production creates a sludge waste, and CDDs/CDFs have been measured in these sludges. For the most part, these sludges have been disposed of in either on-site or off-site RCRA Subtitle D solid waste disposal facilities. However, given the potential for leaching of the heavy metals from the sludge in the Subtitle D landfill, EPA has listed this waste as hazardous waste under Subtitle C. These sludges are now considered a hazardous waste under RCRA and must be disposed of in permitted landfills (U.S. EPA, 2001f).

Fortunately, there has not been any discussion on the dioxin or for that matter other conventional pollutants like heavy metals or aromatic hydrocarbons from KMML. The only studies available are from the university geologists on the heavy metal contamination of ground water.

While concentration of all the hazardous substances in the main products (titanium pigment, nano-kermex and sponge) will be minimal, most of them will be distributed in the gaseous, liquid and solid wastes. Estimates of heavy metals, radionuclides and polycyclic aromatic hydrocarbons generated at the present production level at KMML are given in tables 1,2 and 3. Dioxin and furan found in wastes from titanium processing plants in USA is given in table 4.

Acidity is the only hazard, says KMML

There are mainly two solid waste streams in KMML (i) iron chloride/oxide in the synthetic rutile line and (ii) the effluent treatment plant sludge from the titanium dioxide pigment plant. Incidetnally, the major ingredients in both the stream are the metals other than titanium contained in the feedstock. Until 2001, the waste from the chlorination plant (generating synthetic rutile) ferric chloride, which was highly acidic, containing a portion of the heavy metals in the feedstock used to be disposed off without any further treatment. In 2001, an acid regeneration plant, which would recover hydrochloric acid from ferric chloride waste started functioning. Since then, the acidic waste is being neutralized. In a meeting held at Thiruvananhapuram on 12 Nov 2014 to discuss the causes and solutions for KMML's crisis, the company's technical manager asserted that only wastes that are acidic are hazardous and the neutralized ones are not, and they being non-hazardous can be sold-out or disposed off without any treatment.

Dioxin – Still a hypothesis

Sixteen years after the US EPA and other scientific bodies concluded that the chlorination process in the titanium industry is a major source of dioxin and furan and 12 years after the major players initiated preventive measures and remediation and started paying compensation to the victims, KMML considers this as a hypothesis and wants to "explore whether the highly toxic dioxine is generated during the production process of KMML and if *found* so, methods to be found for avoiding this". For this "a letter was sent to the National Institute of Inter Disciplinary Science and Technology, Thiruvananthapuram for making a study on this and suggest necessary preventive measures for avoiding this (letter attached as Annexure E)".[7]

Recycling Hazardous Wastes

KMML or the Kerala State Pollution Control Board has not published any detailed analysis of the wastes accumulating in the plant premisers or the effluents discharged to the water bodies. With half a million tons of solid waste, which is moving alongwith the groundwater, KMML is now selling a pipe dream of using the waste for making bricks and cement.[8] The Vellore Institute of Technlogy and the National Council for Cement and Building Materials (NCCBM) are conducting laboratory studies on these. In 1998**, KMML had done "commercial production of bricks from the waste Iron Oxide an innovative development by in-house R&D"[9]. These were used for construction of buildings inside the factory. Cement production will cause exposure to heavy metals and dioxin to workers in cement factories and construction industry and also the future occupants of those buildings.**

This is an old idea, they borrowed from DuPont USA. DuPont sold their iron oxide waste as a product called Sierra-Crete which was laid below 58 km of asphalt for roads in new housing developments, parking lots, and school playgrounds in California between 1989 and 1996. About 15 years ago, residents noticed black ooze coming out of the cracks of their streets, ooze that would later turn white. After two lawsuits were filed with the County Supreme Court, a study determined those at highest cancer risk from this exposure are road maintenance workers. Eventually, in January 2005 DuPont agreed to pay about $11.5 million to seal and repair prematurely aging streets where the compound was used.[10] It appears that enemies of KMML have infiltrated the rank of decision makers.

Long Distance transportation to CTSDF, Ambalamugal, Kochi

There are plans to move an estimated 5 lakh tons of solid waste containing dioxin and heavy metals, lying at the KMML compound are leaching into the groundwater for disposal at the Centralized Toxic Substances Disposal Facility (CTSDF) at Ambalamugal.[11] This will involve a total travel of 2x150 lakh km. Considering the highly hazardous nature of substances in the waste and the possibility of accidents, spillages etc, this does not appear to be a sound decision. Since the waste will move out of the private domain, there has to be open discussion based on verifiable and reliable data followed by an environmental public hearing with all the stake holders including road users.

Global Experiences

The Henderson Factory of Titanium Metal Corporation of USA

On 14th May 14, the Las Vegas Journal reported that "one of the world's largest titanium manufacturers has agreed to pay a record $13.8 million penalty for producing and dumping banned cancer-causing chemicals at its Henderson factory. Under a settlement with federal regulators, Titanium Metals Corporation (TIMET), also agreed to perform an extensive investigation and cleanup of potential contamination from the unauthorized manufacture and disposal of PCBs at its 108-acre site on Lake Mead Parkway. According to the Department of Justice and the U.S. Environmental Protection Agency, TIMET's penalty is the largest ever imposed for violations of the Toxic Substances Control Act at a single facility. The corporation will pay another $250,000 for violations related to illegal disposal of hazardous waste water. TIMET's violations stem from EPA inspections in 2005, 2006 and 2008 that showed the company had been illegally producing PCBs as a byproduct of its titanium manufacturing process and disposing of the banned chemical in a solid-waste landfill and a trench at the plant. The company was also accused of illegally dumping acidic, corrosive water into an unapproved waste pond at the facility.[12]

Tronox Incorporated, USA

On November 29, 2010, the multi-national chemical company processing titanium, Tronox Incorporated, has agreed to resolve its environmental liabilities for $270 million and 88 percent of Tronox's interest in a pending litigation. Tronox and 14 of its affiliates filed for protection under Chapter 11 of the U.S. Bankruptcy Code on January 12, 2009 in the U.S. Bankruptcy Court for the Southern District of New York. At the time of the bankruptcy filing, the company was potentially responsible for past costs incurred and future response costs under the Comprehensive Environmental Response, Compensation and Liability Act, CERCLA, commonly known as the Superfund Law, and the Resource Conservation and Recovery Act relating to sites throughout the country, as well as for penalties under CERCLA, RCRA, the Clean Air Act, and the Clean Water Act. Under the terms of the settlement, Tronox will pay $270 million in cash. The bankruptcy settlement will reimburse the EPA for past cleanup costs and fund future cleanups at contaminated sites across the country.[13]

The Dupont's Dioxin legacy in USA

Dupont, a multinational with titanium processing plants in USA, Europe, China and Taiwan has also been at the receiving end for deception and deceit. They diluted the titanium plants solid waste by lime making dioxin waste detection difficult but not impossible. The DuPont company suspected contamination in ferric chloride processing even before well before marketing it later admitted to their employees and to the government that 2,3,7,8 TCDD Dioxin, the most toxic chemical ever made by man, is in their ferric chloride process.

Black foam. This toxic foam was discovered and analyzed by a young Edge Moor mechanical engineer in the early 1990‟s and it was found again recently at the DeLisle, MS TiO2 plant. This light weight material floats to the top of ferric and ferrous chloride carrying dioxins and dioxin like chemicals. The black polymeric foam can be easily dried and exposed dioxin piles can be blown towards peoples homes.

The Edge Moor plant disposed of 41,097 grams of dioxin-laden waste in 2003, which has gone into a unique off- site landfill owned by DuPont located on Cherry Island. Edge Moor TiO2 waste, often called Iron Rich has accumulated into a 500,000-ton pile in what Wilmington, Delaware residents call their “backyard.” The pile (which DuPont originally planned to sell as construction filler) was declared hazardous in 2001 by the EPA because of the presence of hexachlorobenzene, manganese and arsenic, along with dioxins.[14]

DuPont agreed to pay $500,000 to settle state and federal accusations the company polluted the Delaware River with toxic industrial chemicals "numerous" times in the last six years. The U.S. Environmental Protection Agency, Delaware's environmental agency, and state and federal prosecutors joined in a consent decree to curb illegal chemical discharges at DuPont's Edge Moor works next to Fox Point State Park just north of Wilmington, which processes titanium dioxide, used in auto paints, printing, and other industries. DuPont let hydrogen chloride, titanium tetrachloride, iron chloride, titanium ore, and overflow wastewater treatment chemicals into the Delaware, the government said. The company violated permit limits on discharging suspended solids, acids, iron, foam, contaminated storm water, and other pollution.[15]

Conclusion

This medium sized industry with an annual production of less than 40,000 tons of titanium pigment could be a major contributor to the national dioxin inventory. The total environmental load also include more than two dozen hazardous metals and chemical compounds. A large portion of the groundwater has already been contaminated and the management is contemplating of alternate sources for process and domestic water from a stream nearby. The high population density around the factory, proximity to a major fishery and marine export hub in the Arabian sea coast makes the situation highly vulnerable. Thousands of down-winders are suffering from diseases and disabilities, which they attribute to the emissions from the factory. Eminent politicians within the government and the opposition are supporting their demand for proper rehabilitation. Detection of even a pico-gram of dioxin in fish can lead to collapse of the region's fishery exports. At this juncture, the business as usual attitude of the management, the regulator and the government, can be detrimental to the health and livelihood of large number of people and even for the survival of the industry. The need of the hour is an unbiased and objective assessment of the environmental burden from KMML and its effects on the food chain. **As the cost of remediation and rehabilitation is likely to be well-beyond the capacity of the industry, the KMML site has to be declared as a national sacrifice area, in line with the Super Fund sites in USA. The victims of pollution-caused diseases and disabilities and those who are exposed to the chronic releases of toxins through air and water should be compensated and rehabilitated. The cost of compensation and remediation will be very high and beyond the budget of the company. This may be shared by the industry and the state and the central governments.**

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Conflict of interest: None declared

Table -1 :TOXIC METALS GENERATED IN A YEAR – KMML

Source	Element	Generated in a year kg
1 Ilmenite, Petcoke, Sand	Chromium	16011
2 Aluminium chloride. Caustic soda, H2SO4, PetCoke	Nickel	2423
3 Petroleum Coke	Cobalt	1244
4 Petroleum Coke	Magnesium	890
5 Aluminium chloride. Caustic soda, H2SO4	Copper	64
6 do- -do-	Lead	64
7 Petroleum Coke	Barium	25
Total		20721

TABLE 2. DISTRIBUTION OF RADIONUCLIDES IN KMML BENILITE PROCESS

Material	Annual Use Tons	Proportion of total Activity %		Activity Concentration Bq	
		Thorium232	Radium228	Thorium-232	Radium-228
Ilmenite	80000	100	100	6.84E+010	6.12E+010
Iron oxide waste	32000	76.6	45	4.90E+010	2.78E+010
Non-iron waste	1000	18.4	9.2	1.37E+010	6.48E+009
Liquid effluents		5	45.8	3.42E+09	2.80E+010

Source: IAEA, 2012 SAFETY REPORTS SERIES No. 76RADIATION PROTECTION ANDNORM RESIDUE MANAGEMENT" Table 9, p 32

Table 3: Poly Cyclic Aromatic Hydrocarbon: Concentration IN PETCOKE

Compound	Concentration ppm	Kg in one year
2- Methylnaphthalene	2.5	61.8
Anthracene	0.66	16.3
Benzo(a)anthracene	2.2	54.4
Benzo(a)pyrene	2.2	54.4
Benzo(b)fluoranthene	1.1	27.2
Chrysene	2.3	56.9
Dibenzo(a,h)anthracene 0.99	0.99	24.5
Dibenzifloran	0.2	4.9
Indeno (1-2-3-cd) pyrene	0.56	13.8
Fluorene	0.31	7.7
Naphthalene	1.6	39.6
Pyrene	1.7	42.0
Benzo(g,h.,l,)perylene	1.4	34.6
Total PAHs in petroleum coke	21	519.3

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Table -4 : DIOXIN/FURAN IN ANALYTICAL STUDIES IN SAMPLES IN US TITANIUM PLANTS

Ser	Sample	ng/Liter
1	Millennium Baltimore, MI-SO-01,Filter press solids (RIN 4)	2615
2	Millennium Baltimore, MI-WW-01,Chloride solids/waste acid (RIN 1)	812
3	The Millennium Baltimore chloride solids/waste acid (RIN 1, MI-WW-01)	812
4	DuPont New Johnsonville, DPN-SO-01, Wastewater treatment solids:	402
5	DuPont wastewater treatment solids (DPN- SO-01)	402

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Table – 5 RAW MATERIALS USED BY KMML

Material	Formula	Annual Use (Tons)
Silica Sand	SiO2	1200
Sodium Silicate	Na2O3Si	3280
Beneficiated Ilmenite	FeTiO3	4644
Hydrated Lime	*Ca(OH)2*	12800
Aluminium Chloride	AlCl3)	950
Sulphuric Acid	H2SO4	1800
Potassium Chloride	Kcl	114
Petroleum Coke – Npf Grade	C, S, H	6228
Hydrochloric Acid	Hcl	24537
Liquid Chlorine In Containers	Cl2	8043
Caustic Soda Lye	NaOH	3400
Raw Ilmenite	FeTiO3	80000
Floculant		11330
Cabosil	SiO2	1.9
Trimethylol Ethane (trimet)	C8H12O6	240
Zirconium Orthosulphate	O8S2Zr	300
Tri Iso Proponol Amine	**C9H21NO 3**	27
Succinic Acid	C4H6O4	6
Furnace Oil 1000 ltrs	CH4	28029
Liquified Petrolium Gas	C3H8	4000
Aluminium Hydrate	*Al(OH)3,*	1280
Calcined Petroleum Coke	C, S, H	18500
Total		210710

http://kmml.com/php/rawMaterials.php?linkid=57

Note: The above estimates are based on the raw material consumption data provided by KMML in its website.

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