Resource Recovery from Sludge Generated from Dyes and Dye Intermediates Industries through Utilisation in Cement Plant

Vinoth Balakumar, V Kannan, PV Kiran Ananth
Confederation of Indian Industry (CII) Godrej Green Business Centre, Hyderabad, India

Palash Kumar Saha, Dr. Kåre Helge Karstensen
SINTEF, Norway

Abstract

The Indian cement industry has made significant efforts to reduce its carbon footprint by implementing various energy efficiency and environmental measures. Today, the total direct CO_2 emissions stand at 588 kg CO_2/t cement, reduction of 5% compared to baseline year 2010. The emission reduction target of 2020[1] were achieved in 2017 itself, three years ahead of the schedule.

The main levers for reduction have been increases in alternative fuel use, reductions in clinker factor and capacity addition of waste Heat recovery system (WHRS). Alternative fuel use, measured in terms of thermal substitution rate (TSR), increased from 0.6% in 2010 to 3+% in 2017. More than 60 cement plants have been regularly utilizing wastes to substitute conventional fuels such as coal[2].

CII - Godrej GBC, in partnership with Cement Manufacturers' Association (CMA), is working on the initiative to facilitate the use of urban & industrial wastes as Alternative Fuels and Raw materials (AFR) in the Indian cement industry. The three main areas of work are Policy Advocacy, Technical Research & Development and Capacity Building. The CII-GBC website (www.ciiwasteexchange.org) on waste exchange is an attempt to bring all stakeholders together and offer sustainable solutions for waste management in the country.

This paper elaborates the case of gainful recovery of the resource value present in sludge, a hazardous waste generated from one of the major dyes and dye intermediates industries in Vapi, Gujarat (Micas Organics Limited) in a local cement plant (Digvijay-Jamnagar cement plant) in Gujarat as gypsum substitute and the replication potential.

The plant scale trial was conducted under the "Sustainable and Environment-friendly Industrial Production" (SEIP) project which is a joint project of the MOEFCC and GIZ. SINTEF activities in Vapi was a part of its ongoing four-year project (January 2017- December 2020) in India titled- 'Co- processing of Alternative Fuels and Resources in the Cement Industry - Phase II', focusing on providing professional technical assistance on waste related issues and reducing local pollution and exposure to hazardous chemicals – leachates, emissions of methane from landfills and releases to rivers. Confederation of Indian Industry – Sohrabji Godrej Green Business Centre (CII - GBC) has assisted SINTEF in carrying out feasibility studies and plant scale trial in Vapi.

During the plant scale trial, 20 tonnes of sludge could be used in 20 hours (at the rate of 1 tonne/hour) which could substitute equivalent quantity of marine gypsum (16% substitution) without any significant deviations in process and cement quality parameters. Further analysis reveals that there is a potential to substitute as high as 14% of the total Gypsum in Gujarat's cement plants (~ 23 million tonnes of cement capacity[3]) with the sludge generated by the dyes and dye intermediates industries at Vapi, Gujarat.

[1] Voluntary target set by the Indian Cement sector as part of Low Carbon Technology Roadmap
[2] Low carbon technology roadmap for the Indian cement sector: Status review 2018
[3] CII- GBC Database

Introduction

The Vapi industrial area (Gujarat), situated 180 km north of Mumbai, has earned the reputation of being one of the most polluted industrial stretches in the country, with both air and water being deeply contaminated. This estate is considered as the largest industrial region of Gujarat state, with more than 1,500 industries[4]. Industries have started to make significant progress towards upgrading their environment management system Even though the Comprehensive Environmental Pollution Index (CEPI) scores calculated by CPCB have reduced from 90.7 in 2011 to 68.2 in 2016; there remains much scope for improvement

Sludge Generation and Current Management Practices

There are more than 30 dyes and dyes intermediate industries in the Vapi industrial area. Concentrated Sulphuric acid and Oleum are principal raw materials for manufacturing dyes and dye intermediates. These industries are potentially generating 600 to 700 tonnes/day of spent sulphuric acid. The purity of the sulphuric acid in the spent acid is approximately 20%. Low acid content, color and organic impurities are limitations for recycling the effluent.

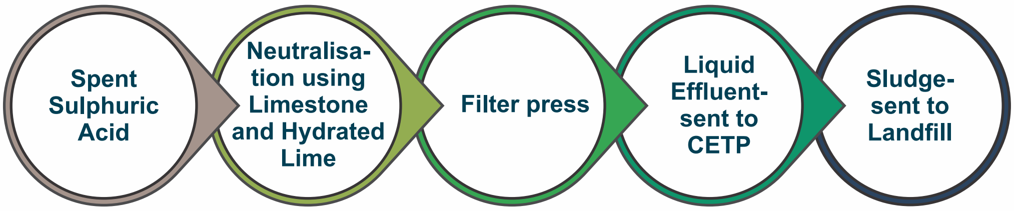

Figure 1: Process of sludge generation from spent sulphuric acid

Part of the spent acid is collected by the distributors, but due to low demand, most of the waste must be managed by the generator. The spent acid can be re-used in other industries such as textiles and alum manufacturers depending on strength, color, and other properties. Only a few generators are sending the spent acid to common effluent treatment plants; others are managing the waste with the in-house set-up.

The left-out material, which is not recyclable or reusable, will be further treated. Gypsum slurry will be generated when the spent sulphuric acid containing organic compounds is neutralized using limestone and hydrated lime. On an average, for every tonne of spent acid will generate 0,5 tonne of sludge; rest is high COD wastewater which is treated in common effluent treatment plant. Therefore, the potential generation of sludge is estimated as 300-350 tonnes/day. But reported generation is only 100-120 tonnes/day, mostly from DCB plants (3, 3 dichloro benzidine dihydrochlorides) such as Micas, Aarti and Himani. Part of spent acid may end up as wastewater which also explains the low quantity of sludge reported. Sludge is a hazardous waste.

GPCB has taken various initiatives and provided platforms to the hazardous waste generators, facility operators and the cement industry for the adoption of waste utilisation in cement industry. In Gujarat, during April 2011 and October 2016, 1.02 Mt of sludge (gypsum substitute) has been utilised in cement plants. But still significant quantity of the sludge is presently sent to landfills. For example, more than 15% of all wastes received at the hazardous waste landfill (TSDF) in Vapi is the sludge generated from dyes and dyes intermediate industries.

The landfill is operated by Vapi Green Enviro Limited – formed by the Vapi Industries Association (VIA) on co-operative principles. The landfill has a capacity of landfilling 1.4 million tonnes of hazardous waste; more than

[4] *http://www.myvapi.com/history.php*

90% already filled. If the landfill receives wastes at the present rate, it will be filled in less than a year[5].

If recoverable materials are put into landfill sites, more energy and resources are used to produce new materials, so landfill sites should not be the first priority for materials with resource recovery potential.

Procedures Followed for the Plant Scale Trial Run in Cement Plant

The plant scale trial was conducted under the "Sustainable and Environment-friendly Industrial Production" (SEIP) project which is a joint project of the MOEFCC and GIZ. SINTEF activities in Vapi is a part of its ongoing project in India titled- 'Co-processing of Alternative Fuels and Resources in the Cement Industry - Phase II', focusing on providing professional technical assistance on waste related issues and reducing local pollution and exposure to hazardous chemicals – leachates, emissions of methane from landfills and releases to rivers. CII - GBC has supported SINTEF in carrying out feasibility studies and plant scale trial in Vapi.

CII-GBC had organised a meeting with plant head, operations head and other officials of Digvijay cement plant (Votorantim Cimentos Group) in Jamnagar to initiate discussions about utilising priority waste streams from Vapi industrial area including the sludge from dyes and dyes intermediate plants. The plant officials had attended the co-processing workshop organised by GIZ, SINTEF and Gujarat State Pollution Control Board (GPCB) in April 2018 with participation of the major industries from Vapi and major cement players in Gujarat.

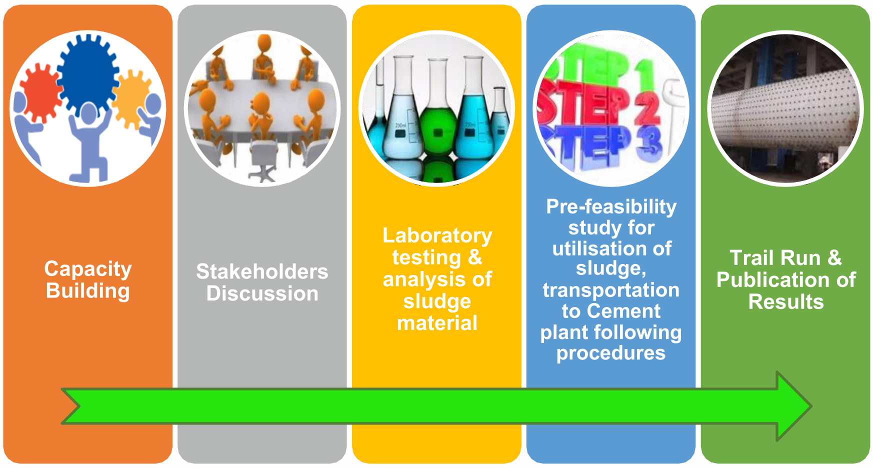

Figure 2: Procedure followed for conducting the trial run of sludge in the cement plant

As a follow up of the workshop, the samples of the sludge from Micas Organics Limited were collected and provided to the laboratory of Digvijay cement plant for analysis. The laboratory tests revealed that the sludge from Micas could be gainfully utilised as a substitute of marine gypsum. During the cement manufacturing process, upon the cooling of clinker, a small amount of gypsum is introduced during the final grinding process to control the setting of cement (retarding agent).

Table 1: Comparison of the sludge from Micas Organics Limited and the marine gypsum

	Unit	Marine gypsum* (Conventional)	Sludge from neutralisation of spent sulphuric acid
SO_3 content	%	34.90	38.52
Purity ($CaSO_4.2H_2O$)	%	75	82.8
Moisture content	%	8.0	21.76
Chloride content	%	<2	<2

Marine gypsum is recovered from salt pans during production of common salt in coastal region, particularly in Gujarat and Tamil Nadu.

[5] *Green Enviro Limited, Vapi*

Micas has adequate facilities for handling and neutralisation of spent sulphuric acid such as storage tanks, covered shed, unloading area, slurry preparation tanks with mechanised system, system for de- watering of sludge, leachate collection pit etc. The wastewater from the neutralisation process is sent to common ETP in Vapi.

One truck containing 20 tonnes of sludge was sent by Micas through a GPCB authorised hazardous waste transporter. The manifest system of the Hazardous and Other Wastes Management and Transboundary Movement Rules (2016) was followed for traceability of the sludge. CPCB has already approved utilisation of spent sulphuric acid containing organic compounds generated from dyes and dyes intermediates units as chemical gypsum for use in cement plants.

The procedure for the trial was discussed and it was mutually agreed that the trial will be undertaken late October after the monsoons.

Plant Scale Trial for Utilization of Sludge

In Digvijay cement plant, the sludge was divided into two batches of 10 tonnes each. One batch of 10 tonnes of sludge was mixed 50 tonnes of marine gypsum (16% material substitution) with the help of a payloader. The mix of sludge and marine gypsum- 60 tonnes in total, was fed into the cement mill hopper and gainfully used in the cement manufacturing process in a course of 10 hours. The material moisture was around 22%. Proper procedures were followed in storage, handling and feeding of material in cement mill. The same procedure was applied for the second batch of 10 tonnes of sludge.

The mixed gypsum (marine gypsum and sludge) of nearly 120 tonnes was fed in to cement mill hoppers. The cement produced in the mill was Portland Pozzolana Cement (PPC). The gypsum from the hopper is passed through weigh feeders and sent into the mill along with clinker. The total material is consumed within nearly 20 hours from the start of the trial.

No abnormalities or deviations are observed in the operation parameters of the mill as well as the pre- grinder. The operating parameters of the cement mill and pre-grinder are tabulated below. In both cases, the production level and additive consumption remains the same. The other process parameters were also within the limit during the utilization of sludge as additive.

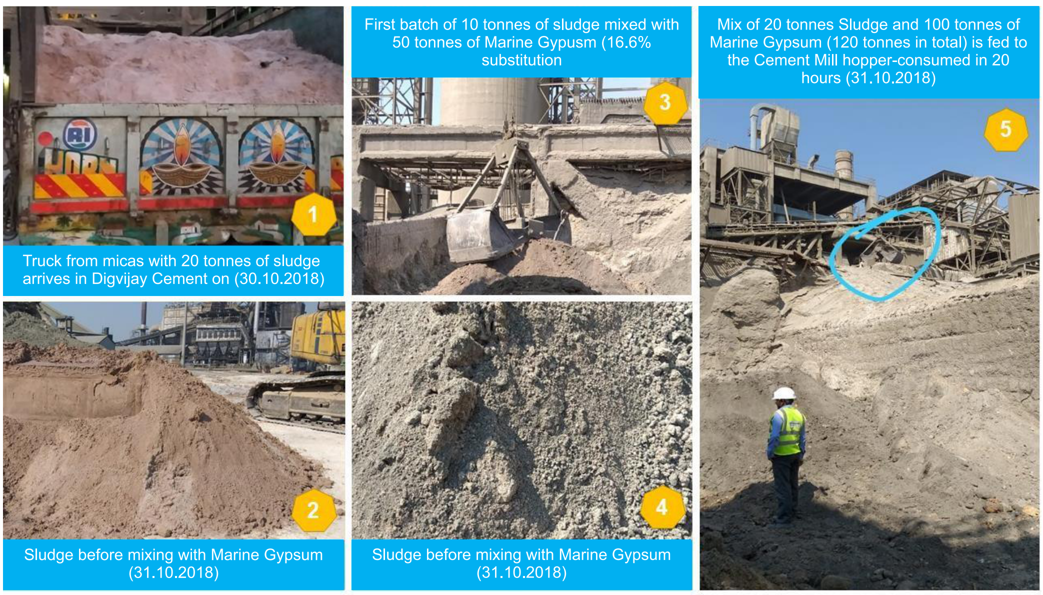

Figure 3: Steps of utilisation of Sludge in Digvijay-Jamnagar cement plant

Table 2: Comparison of the sludge from Micas Organics Limited and the marine gypsum

	Unit	Before Trial	During Trial
Pregrinder parameters			
Pre-grinder load	kW	980	989
Pre-grinder discharge elevator load	kW	64	69
Pregrinder bag house fan speed	rpm	280	290
Bagdouse differential pressure	mmwc	70	70
Pregrinder working pressure	MPa	6.5	6.5
Cement mill parameters			
Separator speed	rpm	630	625
Bag house fan speed	rpm	650	655
Cement mill load	kW	2820	2850
Feed rate			
Pregrinder inlet	tonnes/hr	170	172
Gypsum	tonnes/hr (% of cement)	11.39 (6.7%)	11.18 (6.5%)
Pond fly ash	tonnes/hr (% of cement)	15.3 (9%)	15.48 (9%)
Dry fly ash	tonnes/hr (% of cement)	40.8 (24%)	41.28 (24%)
Clinker feed	tonnes/hr (% of cement)	102.51 (60.3%)	103.2 (60%)
Cement mill inlet	tonnes/hr	230	230

Table 3: Analysis of the Pozzolana Portland Cement (PPC) produced before and during trial

	Unit	Before Trial	During Trial
Chemical properties			
Al_2O_3	%	11.99	12.22
CaO	%	45.48	44.29
Fe_2O_3	%	7.71	7.63
MgO	%	2.13	2.25
SO_3	%	2.52	2.40
SiO_2	%	27.28	28.25
Physical properties			
Specific surface	m2/kg	375	342
Soundness- Le Chatelier	mm	1	1
Setting time- initial	minutes	130	140
Setting time- final	minutes	175	190
Compressive strength - 1 day	Mpa	13.9	13.0
Compressive strength - 3 day	Mpa	27.8	25.6
Compressive strength - 7 day	Mpa	35.9	33.8
Compressive strength - 28 day	Mpa	52.3	49.2

Before trial: PPC produced with Marine Gypsum;
During trial: PPC produced with Mixed Gypsum (Marine Gypsum and Sludge)

The quality of Portland Pozzolana Cement (PPC) produced with mixed gypsum (marine gypsum and sludge) was analyzed and compared with the PPC produced with only marine gypsum.There is no significant change in the chemical or physical properties of the cement produced in both scenarios.

The Outcome & Benefits

The success of the present plant scale trial demonstrates that >15% of the gypsum can be easily substituted by sludge generated from dyes and dyes intermediates industries, with acceptable levels of variation in cement process and quality parameters. If some of the limiting constituents such as colour and moisture content are controlled, the level of utilisation can theoretically reach near 100%.

The cost of gypsum accounts for only 2-3 % of cement costs but the rising demand for cement (and therefore, gypsum) coupled with increasing costs of imported gypsum from Thailand, Oman, Iran etc, have been putting a heavy strain on the industry.

The Indian cement industry has consumed more than 280 million tonnes of gypsum in the last 15- years[6], and the total reserves/resources of mineral gypsum in India as in the year 2015, have been estimated at 1330 million tonnes - 37 million tonnes placed under 'Reserves' category and rest under 'Remaining Resources' category[7]. Estimates reveal that India imports 4.35 million tonnes of natural gypsum annually, making it the largest importer of natural gypsum in the world[8]. The cement industry is therefore exploring alternative sources of gypsum.

[6] *Global Gypsum: https://www.globalgypsum.com/magazine/articles/732-future-asian-gypsum-demand-and- supply-trends-oman-emerging-as-most-significant-source-in-asia*
[7] *Indian Minerals Yearbook 2018, Indian Bureau of Mines*
[8] *Global Gypsum: Future Asian gypsum demand and supply trends*

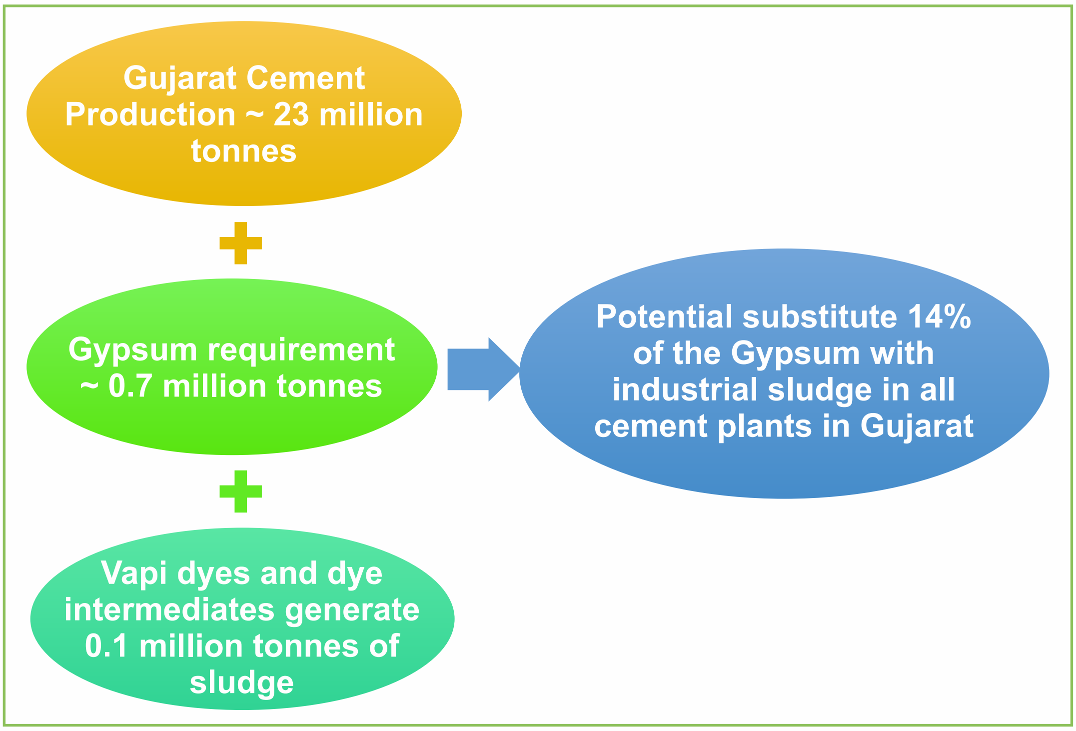

Figure 4: Potential to substitute industrial sludge in Gujarat cement plants

By continued integration of the co-processing and treatment of wastes in energy and resource intensive industry, industrial estates/zones can forego or significantly reduce investments in costly waste incinerators; reduce land requirements for new landfills or increase life of existing landfills, save large amounts of non-renewable fossil fuels and virgin raw materials; reduce greenhouse gas emissions; increase waste treatment capacity and reduce exposure and negative impacts of hazardous chemicals.

Limitations

The perceived limitations for higher utilisation of sludge are (1) colour due to the presence of phenolic and other organic compounds and (2) moisture content (20-25%). The batches of spent acid with acceptable colours for cement production could be separately neutralised and earmarked for utilisation in cement plants. The moisture content could be reduced to less than 10% by solar/sun-drying of the sludge.

The sludge from the Dyes and Dyes Intermediates plants may have residual organic content and therefore, the possible formation of volatile organic compounds (VOCs) should be assessed before feeding the cement mills.

Conclusion

The major cement plants in Gujarat produce close to 23 million tonnes of cement every year. If we conservatively assume that gypsum consumption is 3% of the cement produced, the industry would require 0.7 million tonnes of gypsum every year. The Vapi industrial area potentially generates 0.1 million tonnes of sludge which is equivalent to 14% of the total gypsum required by the cement plants in Gujarat.

India accounts for approximately 16% of the world's dyes production[9]. Since the waste generated from the process is proven to be an effective alternative material, mapping of dyes and dye intermediates industries with cement plants can be explored all across the country.

The possibility of sending spent acid from Vapi directly to the cement plants in Gujarat could be explored in the future. Cement plants have ample limestone which could be used for neutralization of spent acid and production of gypsum substitute. This will reduce the overall cost for operation and material usage. For example, Vatva Acid Bank (Acid Bank Initiatives) is already sending spent acid to Shree Cement in Rajasthan.

A techno-commercial feasibility study for utilizing chemical gypsum in cement plant has to be conducted. CPCB in June 2016 has already published the 'Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule 9 of the Hazardous and Other Wastes (Management and Transboundary movement) Rules, 2016'. CPCB should also lead the development of a viable financial model after discussions with the relevant stakeholders. This would help in creating a win-win, sustainable and replicable solution for the (hazardous) sludge management through resource recovery in the Indian cement industry- a transition towards a circular economy.

Acknowledgement

*We are thankful to **Shree Digvijay Cement Company Limited, Gujarat, Micas Organics Limited, Vapi and GIZ** for all the support & co-operation extended for the plant scale trial.*

[9] *Indian Brand Equity Foundation (IBEF)*