

# Case Studies to Recycle Materials from the Manufacturing Industry

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## Abstract

Three different case studies are presented in which spent materials looked at as wastes for many years, were successfully recycled and thus revalorized. The success factor to reuse spent sodium nitrate, which is a form of “liquid oxygen” for micro-organisms, was the set up of a laboratory plant, convincing the potential partners of the feasibility of the process. In a second application, incineration residues were recycled in huge amounts as a substitute for caustic soda after a detailed analytical assessment of potential pollutants. In a last example, a technical solution allowed the reuse of spent phosphoric acid. Because it contained trace amounts of toluene, a method was developed to store and safely feed it as a nutrient for industrial effluent treatment plants. In all 3 examples, more than one company was involved, and all cases were economically as well as ecologically highly profitable.

*Keywords:* Revalorization, sodium carbonate, sodium nitrate, phosphoric acid.

## 1 Introduction

Sustainable concepts and technologies are characterized by their low resource consumption including the recycling of energy and materials. In this contribution, we present examples for sustainable solutions recently introduced at industrial production sites. Common to the 3 examples presented below is the strict approach by resource efficient solutions, which are a prerequisite to reduce production related costs, and which are considered as critical success factors for companies producing profitably.

## 2 Reuse of spent nitrate as nutrient and oxygen source

A pigment factory was looking for options to remove 5 to 8 t nitrate/d in the effluent. At the site itself, hardly any organic carbon was present in the waste water. Recycling of the sodium nitrate was hardly economical due to its low aqueous concentration of between 10 and 15 g/l. The most appropriate solution seemed to be a biological treatment, where micro-organisms converted nitrate into harmless nitrogen gas. The disadvantage of this route was the need of about 6 t/d of methanol as energy source and the production of about 6 t of biomass, which had to be disposed of elsewhere. During the planning phase, an effluent treatment plant of a paper factory was identified, which used 600 kg/d urea as a nitrogen source for its effluent treatment and additionally supplemented its aeration tanks with 3 – 6 t/d of liquid oxygen.

Although a collaborative solution for the two companies looked economically very promising, consultants of the paper company could not be convinced that nitrate could replace liquid oxygen as well as the nutrient fed, and thus they considered the

project as too risky. The break-through of the application came with laboratory studies (Fig. 1). Two treatment trains were set-up in the laboratory of the paper company. The effluent of the one treatment train was conventionally aerated with air while the other was just fed with nitrate containing effluent of the pigment factory.



**Figure 1:** Two activated sludge treatment trains consisting of 2 serial treatment tanks followed by a sedimentation tank. The plant on the left was aerated while the plant on the right was fed with nitrate.

The laboratory study revealed within a few weeks that the treatment efficiencies achieved in the two set-ups were comparable. Soon afterwards, full scale trials at the treatment plant were initiated. In addition to the effects expected, the effluent plant manager realised, that the sludge properties improved when nitrate was fed. Due to the successful result, “nitrate mobile” was started. Between June 2000 and March 2002, a total volume of 126'000 m<sup>3</sup> containing 1'800 t nitrate was transported from one site to the other (300 m<sup>3</sup>/d, 14 g NO<sub>3</sub>/l). Nowadays, the two companies are linked by a pipeline. The collaboration saved considerable amounts of resources and is highly profitable for both partners.

### **3 Reuse of sodium carbonate from incineration residues**

A company treated its cellulose fibres after the extraction using peroxides and caustic soda (NaOH). The aqueous residues contain about 25'000 mg/l total organic carbon (TOC). Due to the refractory nature, the compounds were not efficiently degraded in the treatment plant. Thus, the effluents were concentrated in a multi-stage evaporator, and the concentrated liquors of 500'000 mg/l TOC were incinerated for steam production. A waste product of the process was the fly ash, of which about 20 - 30 t/d were discharged for years to the waste water treatment plant. This ash is well soluble, since it is composed of 90% sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 10 % sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>).

As a result of this discharge to the sewer system, the pH at the entrance of the treatment plant was in the range of pH 10 - 11, which is highly unfavourable for sludge with good settling properties. Therefore, the pH of the feed was adjusted using sulphuric acid.

After the detailed analysis of the waste composition and an evaluation of recycling options, the use of 1 kg soda ash (= sodium carbonate) to replace 2 litres of caustic soda (NaOH, 30 %) used to neutralise acid scrubber liquids of incinerators, was identified.

The permit to reuse the ashes was obtained after detailed analytical studies including heavy metals and dioxins. The latter amounted to below the 1.0 ng TE/kg dry substance. In a next step, a pilot trail was initiated to check the feasibility of its application (Fig. 2).



**Figure 2:** A big bag of sodium carbonate ashes is fed at various rates to neutralize scrubber liquors

So far, one user has finished the construction of a 100 m<sup>3</sup> silo and is currently in the process of starting up the feed of the ashes as a neutralizing agent. The investment for the installation to recycle 2'500 t ashes per year and thus replacing 5'400 t NaOH (30 %) will be paid back within less than 2 years.

#### **4 Reuse of phosphoric acid as nutrient for the treatment of industrial effluents**

Phosphoric acid is produced of ores rich in P<sub>2</sub>O<sub>5</sub>. Current costs of a purity of 30 % amount to 25 - 30 US \$/ ton (Jasinski, 2002), and the prize in Europe is at about 500 US \$/t H<sub>3</sub>PO<sub>4</sub> (85 %) for a technical grade. Steen (1998) estimates the availability of

the limiting ores to 100 to 210 years worldwide. Therefore, the prize for this basic chemical is certainly bound to increase.

A chemical company used phosphoric acid in huge amounts due to its property of being free of odours. The spent acid was still of a concentration of between 60 to 80 %. It was disposed of by thermal treatment in a municipal waste incinerator for 800 US \$/t H<sub>3</sub>PO<sub>4</sub>. The phosphate finally ended up in the ash of the incinerator which had to be disposed of at a surveyed landfill site.

Technical grade phosphoric acid can be added as nutrient to industrial treatment plants to balance the C:P ratio for achieving an efficient elimination of organic compounds. The yearly P demand of the most important industrial effluent plants in Switzerland is in the range of 120 t P/year.

The detailed analysis revealed that the spent phosphoric acid was mainly contaminated with toluene, which might lead to explosive vapours in storage tanks. Since, however, toluene is easily eliminated by micro-organisms, the authorities agreed on using the spent acid as a nutrient for the treatment of industrial effluents, provided that it is stored and fed from explosion proof equipment. During the first year, excellent experiences were made and almost 300 t of spent phosphoric acid (equivalent to 58 t P/year) was recycled, which is 0.3 % of the total Swiss P consumption (Schluep et al, 2006). The reuse of the liquid which was regarded for long as a waste finally resulted in considerable cost reductions (0.5 Mio. CHF/year).

## 5 Conclusions

Although resource efficient solutions can not be found for any problems encountered, the awareness for the potential demand of energy and resources must be in the focus of any conceptual engineer. Often, the options for solutions seem to be restricted, but “over-the-company-fence” approaches may reveal unexpected and interesting opportunities as wastes may become useful products.

## References

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