

case study bulletin

CL:AIRE case study bulletins provide a source of information on the characterisation and remediation of specific sites in the UK. This case study bulletin describes the application of Stabilisation/Solidification (S/S) and Accelerated Carbonation Technology (ACT) to contaminated materials at the Avenue Coking Works near Chesterfield.

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Remediation Trial at the Avenue Coking Works Using Stabilisation/Solidification and Accelerated Carbonation Technology

1. INTRODUCTION

This bulletin describes a CL:AIRE Technology Demonstration Project (TDP8) in which contaminated materials from the Avenue Coking Works near Chesterfield were treated using Stabilisation/Solidification (S/S) and Accelerated Carbonation Technology (ACT). This was the second field-scale demonstration of ACT and was undertaken in 2001.

The main objective of the trial was to assess the effectiveness of ACT in treating three different contaminated materials from the site: waste tip, plant area and spent oxide material. The results would be compared against 'traditional' cement-based S/S techniques, to assist in the choice of the optimum treatment process for the site. The ultimate aim of the study was to assess the potential for reusing treated material on the site; consequently, the chemical composition, engineering capability and durability of the treated materials were considered.

This trial was funded by the national regeneration agency English Partnerships through the National Coalfields Programme's £104.5M remediation project for the Avenue site, being delivered by East Midlands Development Agency (emda). It was recognised that the high levels and wide range of contaminants in the materials at the site would be difficult to treat solely using conventional methods in isolation such as S/S, soil washing or bioremediation. This trial provided an opportunity to examine innovative alternatives such as ACT.

2. BACKGROUND TO S/S AND ACT

S/S is a remediation process whereby contaminants are immobilised chemically and physically within a hard matrix. The process describes a group of remediation methods that reduce the mobility of harmful chemicals from contaminated soil, sludge or waste. These methods do not usually destroy the chemicals, but keep them from moving into the surrounding environment.

Cementitious S/S involves the mixing of contaminated soils or wastes with cementitious materials, *in situ* or *ex situ*, and these solidify in the presence of water using reactions similar to those that have been thoroughly studied in connection with concrete technology. Cementitious remediation is a flexible technique in effectively managing a wide range of different contaminant types, including both organic and inorganic species. In addition to dealing with contamination, S/S may also improve the physical characteristics and engineering behaviour of the ground.

Additional information on the use of S/S in the UK can be found on the CASSST and STARNET websites (www.cassst.co.uk; www.starnet.eng.cam.ac.uk). Also, useful guidance has been produced by the Environment Agency (2004) and the British Cement Association on the application of S/S (2004).

Accelerated Carbonation Technology (ACT) is a patented S/S process (Hills, 1997) in which contaminated soil or waste is mixed with a cementitious binder and water in a carbon dioxide atmosphere rather than in air. The resulting reaction is rapid and exothermic and results in the immobilisation of contaminants in a stable product. Engineering properties of the soils can be improved and the pH can be reduced by up to 3 units. ACT remediation is often able to overcome cement hydration inhibitory effects normally attributable to certain contaminants, such as zinc and lead.



Figure 1: Site mixing equipment comprising silo (left) and Pugmill mixer (right).

The first field-scale demonstration of ACT took place in 2000 and was undertaken by the Centre for Contaminated Land Remediation at the University of Greenwich to demonstrate the technology for remediating contaminated land. The research was targeted at inorganic contaminants found within the University-owned Astra fireworks site at Dartford, Kent. The grossly contaminated soil, with high levels of copper and zinc, was successfully remediated to below drinking water limits. The process was shown to be particularly beneficial in granulating the sticky cohesive clay present at the site, suggesting that ACT could be used to improve the engineering properties of poor soils.

3. BACKGROUND TO THE SITE

The Avenue Coking Plant and Chemical Works were constructed in the 1950s and produced 18 million tonnes of smokeless domestic fuel, by-products and town gas until 1992. Prior to this, the site had been host to a colliery, lime and iron works, and also included a former licensed tip and contaminated lagoons. Consequently, extensive contamination was present on the site within tar lagoons, waste tips, site soils, surface and groundwater, tanks, sumps and redundant pipework. The contaminants generally comprised coal tars, lime sludge, acids, phenols, polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOC), spent oxide (commonly known as Blue Billy), ammoniacal substances, heavy metals and asbestos. The site was considered by the Environment Agency to be a polluter of controlled waters including the adjacent River Rother.

The site ceased operations and closed in 1992. It was transferred to English Partnerships' National Coalfields Programme in 1996, and to emda as English Partnerships' delivery agent in April 1999. Jacobs Babbie (formerly Babbie Group) was commissioned by emda as principal consultants in the remediation and redevelopment of the 98 hectare site. Jacobs Babbie identified a number of contaminated materials on the site and managed a series of technology

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demonstrations to see which one would be most suitable for treating the materials. The S/S and ACT trial formed part of these demonstrations and took place in 2001). Three materials were chosen for this trial - the former waste tip, containing a mixture of contaminated material; the plant area, contaminated mainly by organic materials such as phenols, petroleum hydrocarbons and aromatic hydrocarbons; and spent oxide deposits, mainly composed of metallic cyanides. Further site details are provided in CL:AIRE TDP6 Report, "Biopile Field Demonstration at the Avenue Coking Works".

4. DEMONSTRATION TRIAL SUPPORT ISSUES

The Environment Agency exempted the trial from the Waste Management Licensing Regulations (1994) and it was operated within the Construction (Design and Management) Regulations (1994).

The overall contract period was eleven weeks and comprised the following stages:

- Sampling and material characterisation; treatability trials and pilot study;
- Site trials and establishment of the test cells;
- Issue of report to Jacobs Babbie;
- Ongoing leach testing of test cells for three months.

5. LABORATORY TREATABILITY STUDIES AND PILOT STUDY

5.1 COLLECTION AND CHARACTERISATION OF THE THREE MATERIALS

Three stockpiles were created by Jacobs Babbie of each of the three contaminated material streams for treatment; these had been screened to remove large (> 75 mm) stones and blocks of wood and to produce a relatively homogeneous feedstock. An approximately 100 kg sample of each material was taken for the treatability study and pilot study; a representative sample was obtained using a nine point sampling method similar to that given in Annex D of BS 10175. The material was screened to 6 mm in order to avoid damaging mixing equipment.

The contaminated materials were analysed physically and chemically to identify contaminants present and give guidance on the types of binder required and any form of pretreatment or use of additives. The choice of optimum binder was made on the basis of the leaching characteristics of the treated materials.

All three materials contained sufficient moisture to be treated by both S/S and ACT without the need to add extra water. They were all of a coarse granular nature making them compatible with S/S technologies; the plant area material in particular contained a small amount of fine silt-like particles.

Single chemical analyses (to give an indication of contaminants present) of the three contaminated materials showed them to contain low concentrations of arsenic, cadmium, chromium, lead, mercury, selenium, copper, nickel, boron and zinc. Each material exhibited differences with respect to sulphur, cyanides, thiocyanates and organic compounds. The spent oxide material contained more sulphur and cyanide salts compared to the other two and showed a low pH value (<4), typical of this type of material. All three materials also contained relatively high levels of petroleum hydrocarbons (TPH).

The three materials were also subjected to leach testing using the National Rivers Authority (NRA) test protocol (Lewin *et al.*, 1994). This method for producing the leachate involves shaking the sample with deionised water (pH 5.6) for 24 hours and uses a liquid to soil ratio of 10:1.

The results showed that the waste tip and plant area materials leached low concentrations of heavy metals, but that cyanides, TPH and PAH were leached readily from all three materials. In addition, the spent oxide material leached heavy metals such as lead, chromium, copper, nickel and zinc.

5.2 BINDER SELECTION

Binder selection was carried out by using small-scale (i.e. 0.5 kg) studies in the laboratory. These studies showed that the accelerated carbonation treatment was exothermic; this was in contrast to S/S which produced little heat on mixing. Therefore, for ACT only, pilot plant (i.e. 25 kg) studies were conducted to assess scaling up as there were concerns that the high temperatures might affect the degree of carbonation.

The choice of binder was decided by testing various binder/contaminated material combinations and assessing them with respect to leachate analysis using the NRA method. The small-scale mixes were also used to assess the effect of any pretreatments or additives which may be needed to treat any contaminants that are

not adequately treated using the binder alone. These include activated carbon and pulverised fuel ash (PFA) for their absorption potential and hydrogen peroxide as a potential treatment for the cyanides present.

5.2.1 Stabilisation/Solidification

Binders were mixed with the three contaminated materials at 10 % and 20 % dosage levels by weight of the material in a mechanical mixer for 5 minutes and allowed to cure in a sealed container for 28 days prior to leach testing. These dosage levels were those commonly used for soil stabilisation purposes.

Each of the mixes demonstrated different leaching characteristics with respect to cyanide, TPH and PAH and overall the leaching of heavy metals was low, with the exception of Cr. The best binder from those tested was a calcium sulphoaluminate cement. The cement alone was used for the waste tip material, and PFA was added at 10 % dosage for the plant area material, and at 5 % dosage for the spent oxide to improve the engineering properties of the treated materials.

5.2.2 Accelerated Carbonation Technology

Samples were prepared as above, but after mixing for 5 minutes each mixture was exposed to gaseous carbon dioxide at 20 °C for 10 minutes whilst ensuring that the mixer continued mixing so that fresh surfaces were exposed to the gas. At the end of the carbonation period, the samples were placed in sealed plastic bags and tested for leaching using the NRA method as above.

Previous research with accelerated carbonation (see section 2) had indicated that a very finely ground cement was the optimum binder for the process because of its higher reactivity compared with Portland cement.

Similar tests were carried out for all three contaminated materials using accelerated carbonation technology. The results again showed different trends for the different mixes, the main feature being the significantly increased leaching of cyanide from the spent oxide material. Previous studies with a spent oxide material from a gas works site indicated that certain additives had little effect on leaching of cyanide and it was the pH value which had the most effect on leaching, which is a useful lesson for the future application of this technology.

The chosen binders for the field trials were a very finely ground cement, lime and PFA for the waste tip and plant area material, whereas the fine cement alone was used for spent oxide, even though leaching of cyanide was high. Due to time and resource constraints additional laboratory testing could not be carried out to optimise the mixes further.

5.3 PILOT PLANT STUDY

The pilot plant allowed scaling-up of the treatment by a factor of 50 (from 0.5 kg to 25 kg). The equipment consisted of a high-speed mixer capable of handling 80 litres of soil. The mixer had been modified to allow the injection of gaseous carbon dioxide and removal of exhaust gases. Exhaust gases were passed through a carbon filter, which removed any hazardous and flammable organic vapour which may have been released.

The pilot plant was used for the ACT treatment of the waste tip, plant area and spent oxide materials. Thus, 25 kg contaminated material was mixed with binder and additives for 5 minutes prior to a 10 minute injection of gaseous carbon dioxide. The primary mixing stage increased the temperature from 20 °C to 40 °C, due to the friction effect of mixing semi-dry granular material with binder powder. The ACT reaction increased the temperature further by approximately 25 °C. The samples were subjected to leachate testing and the data showed that scaling-up batch sizes had no effect on leaching characteristics.

6. TECHNOLOGY DEMONSTRATION SET-UP

An area of approximately 40 m x 40 m was used for the trials process, with treated material being placed in monitoring cells for post trial and long-term monitoring.

The test cells were of similar dimension, covering a total area of approximately 16 m x 20 m with each cell at a depth of 1.5 m at its deepest end, and lined with impermeable HDPE geotextile liners (Figure 2).

The impact of engineering properties on the effectiveness of the treatment process was assessed by either compacting or loosely placing the treated material within the cells.

Samples were taken from each of the uncompacted cells immediately after placement and then at monthly intervals for 3 months. Each sample was obtained by digging with a hand shovel to a depth of 30 cm and removing approximately 1 kg of material (at this depth) into a container. Three samples were taken from each cell.



Figure 2: Treatment cells before being filled with treated material.

The compacted cells were monitored visually to assess hardness and surface ponding.

All samples were analysed for chemical content and subjected to the NRA leach test. A range of physical classification and durability tests was also undertaken on the samples in accordance with the British Standard BS 1377:1990 (BSI, 1990), including particle size distribution, specific gravity, compaction (2.5 kg), California Bearing Ratio, 10 % Fines and frost susceptibility.

Chemical testing of the treated materials was carried out by ALcontrol Geochem. The soils engineering tests were performed by Exploration Associates.

For the purposes of assessing the relative performance of the materials with respect to leach testing, the New Dutch List was used to provide screening values for the contaminants in the leachate.

7. S/S TRIAL

7.1 TREATMENT PROCESS

Remediation was carried out on a batch-mixing basis with each batch comprising approximately 4 m³ of material. A computerised Pugmill mixer blended the stockpiled contaminated materials with the binder and additive chosen in the treatability study (Figure 1). The spent oxide stockpile became wet from rainwater exposure and could not be handled by the equipment on the site, therefore PFA was mixed with this material at a 10 % dosage to produce a separate stockpile for treatment.

Each contaminated material was mixed with the appropriate binder and additive for 5 minutes and placed in their designated test cells for longer-term monitoring.

All three of the S/S treated contaminated materials were granular in nature initially and then formed monolithic products when compacted in their respective cells. They also formed monolithic products when not compacted (i.e. the discrete particles stuck together), indicating that the hydration of the binder continued over a long period of time. As a consequence, the materials were not subjected to the aggregate-based engineering tests as they would not have produced suitable end material. Thus, the 10 % Fines and frost susceptibility tests were omitted and soils-related compaction tests were carried out instead.

7.2 PERFORMANCE EVALUATION - ENGINEERING PROPERTIES

The samples which were obtained after 28 days from the uncompacted cells all demonstrated typical soil-like characteristics when subjected to the standard compaction test. The classification test results obtained for the treated materials indicated their general suitability for use as engineering fill, in accordance with the Specification for Highways Manual (Highways Agency, 2001).

7.3 PERFORMANCE EVALUATION - CHEMICAL PROPERTIES

The samples taken from the uncompacted cells were subjected to soils analysis and NRA leachate testing; the cells were re-sampled after 1, 2 and 3 months. Some of the cells could not be sampled after 2 months due to heavy rainfall, which covered the surfaces in water. The leachate data were very variable. Therefore, to aid interpretation the data shown in Figure 4 are individual triplicate values rather than mean values.

The results showed that the leaching of heavy metals was generally low with the exception of chromium for the plant area and waste tip materials (Figure 4a), although their respective values decreased with time, which suggested ongoing binder hydration. There was significant cyanide leaching from the spent oxide material, but much less from the waste tip and plant area materials. Generally, the leaching of TPH and PAH was high initially, but reduced over the three month treatment period for all three materials.

8. ACT TRIAL

8.1 TREATMENT PROCESS

The materials that were subjected to ACT were transferred from the Pugmill mixer into the rotating carbonation chamber for exposure to gaseous carbon dioxide for approximately 20 minutes to ensure complete carbonation of the binder. Note that the pilot plant used a 10 minute injection time but this was a more efficient mixer. The gas was added at a controlled rate to the slowly rotating carbonation drum, first purging the air then maintaining a carbon dioxide saturated atmosphere at normal atmospheric pressure for the duration of the carbonation reaction. The carbonation drum rotated at approximately 10 rpm to agitate and keep material continuously exposed to the gas (Figure 3).

During the treatability studies, temperature increases of between 15 °C and 20 °C were obtained for 0.5 kg laboratory batches. The previous ACT trial at Dartford (section 2) gave a higher increase, in the order of 50 °C. Therefore, a similar increase was expected during the treatment of the materials and a two-stage activated carbon filter unit was used to trap any volatile and semi-volatile organic compounds which may have been driven off by the temperature exotherm.



Figure 3: Carbonation chamber (centre) and carbon dioxide storage cylinder (right).

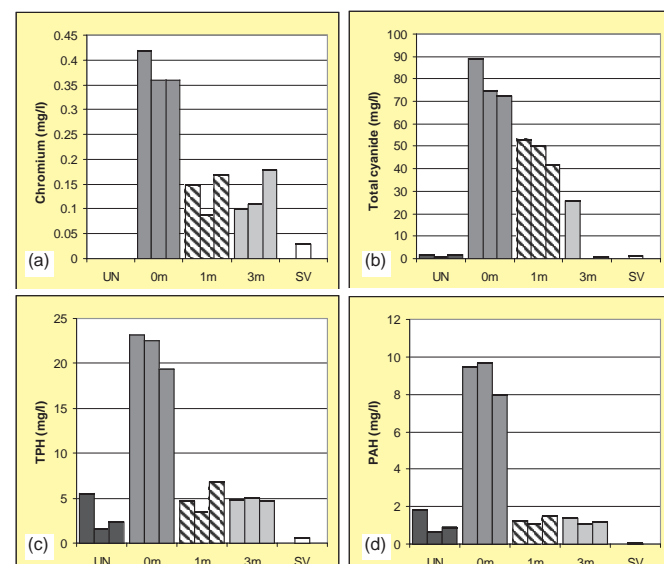


Figure 4: Selected leachate results after 0, 1 and 3 months for (a) Cr and S/S-treated waste tip; (b) Cyanide and ACT-treated waste tip; (c) TPH and ACT-treated plant area; and (d) PAH and ACT-treated plant area. UN represents untreated material and SV are the relevant screening values.

The exhaust gases were monitored using a Multi-Ray (PGM 50) gas analyser both prior to and after the activated carbon filtration unit, to assess quantity and type of emission, and to ensure all emissions were removed from the exhaust stream to maintain ambient air quality.

In contrast to the S/S-treated materials, ACT produced granules, which remained as such even under compaction. These were subjected to the full range of tests in BS 1377, which is relevant to soils that will be used for civil engineering purposes.

8.2 PERFORMANCE EVALUATION - ENGINEERING PROPERTIES

All samples demonstrated typical soil-like characteristics when subjected to the standard compaction test. In all cases the stockpiled materials prior to treatment were of poor quality and generally unsuitable for use as construction materials. The geotechnical testing results indicated that the physical properties of all the treated samples had been improved. The classification, strength and durability test results obtained for the treated materials indicated their general suitability for use, in accordance with the Specification for Highways, as Selected Granular Fill Classes 6C (starter layer) and 6F1 (capping layer).

8.3 PERFORMANCE EVALUATION - CHEMICAL PROPERTIES

Low concentrations (below the screening values) of heavy metals leached from the ACT-treated waste tip material; leaching of chromium was low, unlike its S/S-treated counterpart. However, leaching of cyanide (Figure 4b), TPH and PAH was high, although there was some reduction over the three months. For the ACT-treated plant area material, leaching of cyanide was low, but TPH and PAH leaching was significantly higher than the screening value, but again reduced on ageing (Figures 4c and 4d). The leachate from the ACT-treated spent oxide material was dominated by high concentrations of cyanide which had also been noted during the laboratory trials.

Carbonation is usually accompanied by a rapid increase in temperature (up to 90 °C) and results in a lowering of pH of the treated material compared with an uncarbonated analogue. Whilst the former was observed for each ACT-treated batch, the pH did not decrease as much as was expected, suggesting that carbonation was only partially completed. Thus, the pH of the treated spent oxide and waste tip materials was 11-12 and the pH of the treated plant area material was above 12. The relatively high pH in all the treated materials would have led to solubilisation of the cyanide. Factors that may have been responsible for the partial carbonation include the presence of hydrophobic organic chemicals (e.g. oils) which may have impeded dissolution of carbon dioxide in the water and the high processing temperatures which may have caused the evaporation of too much water during treatment.

9. ECONOMIC CONSIDERATIONS

At the time of the trial, costs were estimated for the treatment of the three contaminated materials using S/S and ACT. The values were based on assumed volumes (300,000 m³ for the waste tip material, including the spent oxide and 80,000 m³ for plant area material) and material densities (1,400 kg/m³) and excluded environmental insurance, the cost of further leaching tests (after treatability study) and of post-completion monitoring and testing. Smaller volumes would increase the cost per tonne, due to the fixed costs associated with mobilisation and setting up of the plant. The estimated costs, an average value taken from the three materials, were approximately £23/tonne for S/S and £45/tonne for ACT.

Both techniques are quite different in their respective mechanisms and should not be directly compared as different binders were employed for the treatment of each material. Binder costs, however, were generally less than £2/tonne and the higher figures for ACT are due to the cost of the carbon dioxide and the associated increased handling costs. More recently, however, it has been suggested that the equivalent 2006 treatment costs for treating the three materials with ACT would be in the order of £25/tonne, due to advances in the technology since 2001 (Hills, personal communication).

10. CONCLUSIONS AND LESSONS LEARNED

The objective of the trial was to investigate the potential of two stabilisation technologies to treat contaminated materials from the Avenue Coking Works and generate materials suitable for reuse on the site. Three complex and heterogeneous contaminated material streams were treated by S/S and ACT and the treated materials were assessed on the basis of their geotechnical and chemical properties.

The chemical composition of the materials showed them to be contaminated with cyanide, petroleum hydrocarbons and PAH. Their heavy metal content, however, was

relatively low. Cementitious S/S is a remediation technology known to be particularly effective in treating soils and wastes contaminated with heavy metals.

Laboratory treatability studies were conducted to select the most appropriate binder for use in the field-scale trials. During these experiments several additives and pretreatments were investigated to enhance the immobilisation of the contaminants. Due to time and resource constraints the chosen binders were not fully optimised with respect to cyanide and organics; they were a compromise solution, being the best choice of the binders tested. As such, it was not unexpected that the field-scale trial did not achieve the desired leaching results. Nevertheless, the trial did prove useful in assessing the geotechnical suitability and the effect of short-term weathering on the properties of the treated materials.

The pilot trial showed that scaling-up batch sizes from the treatability studies had no effect on leaching characteristics.

Of the three contaminated materials, the spent oxide proved to be the most difficult to treat using both stabilisation techniques. Both methods increased the leaching of organic species, and cyanides in particular, compared with untreated material. Similar behaviour was observed for the waste tip material, but the plant area material demonstrated much lower cyanide leaching. In general terms, leaching results after three months were better than those after 0 and 1 months for all contaminants using either treatment method, but were still higher than the untreated material.

Cyanides are very difficult to immobilise and as such usually require their destruction prior to S/S. The materials which required treatment in this trial were not soils, rather they were discrete particulate materials, and it was hoped that these particles could be solidified in such a way as to reduce leaching of the cyanide and organic materials. Overall, this approach was shown to be unsuccessful.

ACT was a new technique that had only been used once before in a large-scale trial, which was with soil contaminated with heavy metals. That trial had indicated that carbonation of the soil/binder mixture had produced material with a pH below that of the uncarbonated mixture. Carbonation of the materials in the Avenue remediation trial, however, resulted in pH values similar to those of the uncarbonated mixtures. In future applications, it will be important to optimise carbonation during the laboratory study, so that the full benefits of applying this method are achieved.

With respect to the geotechnical properties of the treated materials, both ACT and S/S produced granular aggregate, which could be used on the site as engineering fill. The S/S method additionally produced a solid mass on compaction, indicating its potential use in the construction of sub bases for roads.

This trial has highlighted the importance of successful treatability trials with respect to binder selection, choice of additives and pretreatment steps, and optimising carbonation. There is now clear and detailed guidance available for those designing and carrying out S/S trials. It details the use of treatability studies to validate mix designs and site trials to assess the proposed plant and construction methods (Environment Agency, 2004).

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