Electrochemical desalination of salt infected limestone masonry of a historic warehouse

Salt induced decay of porous construction materials can cause severe loss of cultural heritage and can in some cases also develop to structural problems. To get the salts out of the porous building materials in a structure is not a simple task. The present paper reports results from a test scale plant for electrochemical desalination, a method where the driving force is an applied electrical potential. The test plant covered about 25 m² surface of a limestone wall of a historic warehouse. It consisted of 72 electrode units which were placed in two rows; the one above the other and the mutual distance between electrodes was 50 cm. The wall was severely infected with NaCl and the average concentration of chloride was 0.72 wt%. The test lasted for about a year, and 3.8 kg chloride corresponding to 6.3 kg NaCl was removed during this period. The part of the wall underneath the electrodes was successfully desalinated; however, the Cl concentration was in the same level as initially in samples taken just between sets of anodes and cathodes. The desalination was thus not completed during the test. The removal rate for Cl into the anodes was constant all through the test revealing that the desalination could have continued if the test had lasted longer. The test showed that the overall method works, but it also underlined the necessity for development of a new design, which allow for shorter distance between the electrodes in order to shorten the duration of the treatment.

Electrokinetic desalination of sandstones for NaCl removal: Test of different clay poultices at the electrodes

Salt induced decay is a serious threat to many historic stone and brick buildings and monuments. Further salt decay can be problematic in more recent buildings, as well, causing repeated plaster and paint peeling and increased hygroscopic moisture content. There is a need for development of reliable methods to remove the damaging salts in order to stop the decay. Electrokinetic desalination of fired clay bricks have previously shown efficient in laboratory scale and in the present work the method is tested for desalination of Cotta and Posta sandstones, which both have lower porosity than the bricks studied. The stones were contaminated with NaCl by submersion prior to the desalination experiments, where an electric DC field was applied to the stones from electrodes placed in clay poultice. Two poultice types were tested: calcareous clay used brick production and a mixture of kaolinite and calcite. Both poultice types neutralized efficiently the acid from electrolysis at the anode. Regardless poultice and stone type high initial concentrations of chloride (0.41 and 0.34wt%) were reduced to below the target value (0.03wt%) in less than 3 weeks with 10mA (corresponding to about 4A/m² of stone surface) applied. At the end of all desalination experiments the water content in the poultice at the cathode was higher than in the poultice at the anode, revealing electroosmotic water transport. The water profiles in the stones, however, did not indicate electroosmosis as they were quite uniform within each stone, but electroosmosis in the poultices may have caused suction/pressure over the interface between stone and poultice causing the differences in poultice water content. The transport numbers for Cl⁻ and Na⁺ differed in the two stones and were highest in the most porous Cotta sandstone in spite of similar high pore water concentrations and the same applied electric current. The hypotheses is that a layered structure of the sandstones could be the cause for this, as the electric current may preferentially flow in certain paths through the stone, which are thus desalinated first. After the desalination of the paths with lowest resistivity the major charge carrying ion here is then OH⁻ from electrolysis at the cathode slowing down the desalination of the remaining part of the stone.
Electrochemical desalination of historic Portuguese Tiles, Azulejos, in laboratory scale

General information
Publication status: Published
Organisations: Section for Construction Materials, Department of Civil Engineering, Escola Superior Agrária de Coimbra
Contributors: Ottosen, L. M., Ferreira, C., Christensen, I. V.
Publication date: 2011

Host publication information
Title of host publication: Salt Weathering on Buildings and Stone Sculptures
Keywords: Electrokinetic desalination, Nitrates, Tiles, Chlorides, Azulejos
URLs:
http://swbss2011.org/
Source: orbit
Source-ID: 315782
Research output: Chapter in Book/Report/Conference proceeding › Article in proceedings – Annual report year: 2011 › Research › peer-review

Electrochemical in-situ impregnation of wood using a copper nail as source for copper
A new method for copper impregnation of wood in structures was suggested and tested in laboratory scale with specimen of new pine sapwood. A copper nail and a steel screw were placed in the wood, and an electric direct current field was applied, so the copper nail was anode and the screw was cathode. At the anode, copper ions were generated. The copper ions were transported into the wood by electromigration (movement of ions in an applied electric field) towards the cathode, and a volume between the two electrodes was thereby impregnated. Copper also moved to a lesser degree in the opposite direction, probably due to capillary effects, and a smaller volume behind the anode was impregnated as well. The impregnation perpendicular to the grain was limited compared to the one along the grain. The highest Cu concentrations were obtained close to the anode.

General information
Publication status: Published
Organisations: Section for Construction Materials, Department of Civil Engineering
Contributors: Ottosen, L. M., Block, T., Nymark, M., Christensen, I. V.
Pages: 289-302
Publication date: 2011
Peer-reviewed: Yes
Evaluation of Salt Removal from Azulejo Tiles and Mortars using Electrodesalination

Azulejo tiles are part of the Portuguese cultural heritage and are worldwide appreciated. The durability of this building material is affected by the accumulation of salts, causing fractures and peeling of the glazing and ultimately leading to the degradation of the tile panels and the irremediable loss of historic value. In this work preliminary studies with single tiles presenting an underlying layer of mortar have been conducted to assess the amount of salts that can be removed from the building material using a new technique called “electrodesalination”, in which the salt’s ions are transported out from the tiles by applying an electric current on the backside. Results shown here include an assessment of how much of the salts did come out in comparison to what was originally there, and additionally if the electrodesalination succeeded in removing salts down to a point where the tile and underlying mortar are no longer at risk of salt induced decay. The main conclusions are that the technique is successful in extracting salts from mortars (removal efficiencies between 88% and 92%) but not as good for the tile (removals between 10% and 80%). The risk of salt damage to the mortar and tile was either considerably reduced or disappeared, except for one situation with nitrates, thus showing that even though some optimisation is needed, electrodesalination stands as a promising in-situ technique to improve durability of the historic valuable Portuguese Azulejo tile.

General information
Publication status: Published
Organisations: Department of Civil Engineering, Section for Construction Materials
Contributors: Ferreira, C. M. D., Ottosen, L. M., Christensen, I. V., Brammer, S. H., Sveegaard, D. A. F.
Publication date: 2011

Excursions and participation from companies in a weekly 5 ECTS course
A major factor when choosing the teaching methods in a new weekly 5 ECTS course was to enhance the student’s engagement and responsibility for own learning by setting a frame enabling them to visualize themselves as civil engineers. The course is “Materials Durability and Repair” and it is offered to civil engineering students (both at bachelor and master level) as an advanced and elective course. A maximum number of students in the course is set to 25 for practical reasons. Excursions to relevant sites with structures suffering from decay or where repair actions take place was one important teaching method. The excursions took place preferably as introduction to a new part-topic so the students had a common knowledge platform from where the more theoretical teaching could set off. The teachers experienced higher motivation from the students when the excursions were before the lectures on the connected topic than vice versa, probably because the ability to relate the theory to the real life made the topic seem more relevant to them. At the excursions the students took samples which they analysed in the laboratory at the university to enhance the active learning. As these samples are from real sites, they also reflect the huge variability at such sites and sometimes the results did not support the theory. The frustration of not knowing all upfront places the student in a situation well known to working engineers and formed background for relevant discussions. Experts from companies took part in planning of some of the excursions and gave lectures on “real life cases” during the course. This involvement from companies introduced the students to the engineering community which they will join in the future. The companies engagement was important both to the training of scientific engineering skills and professional skills. Also important to the training of professional skills was the deliverables from the students, which was dissemination of own work in articles and a poster presentation performed in groups of 5 students. Student evaluations of the course were positive and currently the course is running for the third time. It is oversubscribed and has a waiting list, underlining the need for such a course.

General information
Publication status: Published
Organisations: Section for Construction Materials, Department of Civil Engineering
Contributors: Ottosen, L. M., Christensen, I. V.
Development of Electrode Units for Electrokinetic Desalination of Masonry and Pilot Scale Test at Three locations for Removal of Chlorides

Electrode units for electrokinetic desalination of masonry has been developed and tested in pilot scale at three different locations. The units are formed as casings with a metallic mesh electrode, and carbonate rich clay to buffer the acid produced at the anode. The case has an extra loose bottom which allows continuous pressure between clay and masonry so good electrical contact is remained. The electrode units were tested at three different locations, two on baked brick masonry (inside in a heated room and outside on a masonry with severe plaster peeling) and the third pilot scale experiment was conducted outside on a limestone masonry. The duration of the experiments was 4-8 month. Chloride concentrations were measured in drilling powder from the masonry before and after experiments. In all three masonries, the average concentrations decreased. The transport numbers for chloride was between 0.33 and 0.48 which shows that the major part of the charge transfer towards the anode was chloride transport, even in the masonry with lowest chloride concentration. The transport number increased in the same order as the initial concentration increased.
Electrokinetic desalination of glazed ceramic tiles
Electrokinetic desalination is a method where an applied electric DC field is the driving force for removal of salts from porous building materials. In the present paper, the method is tested in laboratory scale for desalination of single ceramic tiles. In a model system, where a tile was contaminated with NaCl during submersion and subsequently desalinated by the method, the desalination was completed in that the high and problematic initial Cl(-) concentration was reduced to an unproblematic concentration. Further conductivity measurements showed a very low conductivity in the tile after treatment, indicating that supply of ions from the poultice at the electrodes into the tile was limited. Electroosmotic transport of water was seen when low ionic content was reached. Experiments were also conducted with XVIII-century tiles, which had been removed from Palacio Centeno (Lisbon) during renovation due to damage of the glazing from the presence of salts. These tiles were severely contaminated with both chlorides and nitrates, and one of the tiles also contained sulphates though at a low concentration. The charge transfer was too low in the experiments to obtain full desalination, but promising results were obtained as significant decreases (> 81% Cl(-), similar to 59% NO(3) (-) and similar to 22% SO(4) (2-)) were seen.

General information
Publication status: Published
Organisations: Section for Construction Materials, Department of Civil Engineering, Escola Superior Agrária de Coimbra
Contributors: Ottosen, L. M., Ferreira, C., Christensen, I. V.
Pages: 1161-1171
Publication date: 2010
Peer-reviewed: Yes

Publication information
Journal: Journal of Applied Electrochemistry
Volume: 40
Issue number: 6
ISSN (Print): 0021-891X
Ratings:
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.74 SNIP 0.895
Web of Science (2010): Impact factor 1.496
Web of Science (2010): Indexed yes
Original language: English
DOIs: 10.1007/s10800-010-0086-x
Source: orbit
Source-ID: 281653
Research output: Contribution to journal › Conference article – Annual report year: 2010 › Research › peer-review

Opgradering af farligt røggasaffald

General information
Publication status: Published
Organisations: Section for Arctic Technology, Department of Civil Engineering, Section for Construction Materials, CHEC Research Centre, Department of Chemical and Biochemical Engineering, Arctic Technology Centre
Contributors: Jensen, P. E., Kirkelund, G. M., Ottosen, L. M., Christensen, I. V., Pedersen, A. J.
Pages: 16-19
Publication date: 2010
Peer-reviewed: Unknown

Publication information
Journal: Dansk Kemi
Volume: 91
Issue number: 4
ISSN (Print): 0011-6335
Original language: Danish
Source: orbit
Source-ID: 259729
Research output: Contribution to journal › Journal article – Annual report year: 2010 › Communication

Removal of alum from Iron-Age wooden objects by an applied electric field
In this paper removal of potassium, sulfate and aluminum ions from waterlogged alum treated wood with the use of an applied electric field is described. An electric DC field was applied across the wood for 4-20 days. At the end of the experiments sulfate had moved as expected towards the anode and potassium had moved towards the cathode. One
experiment showed that after 20 days only 10% of the sulfate and 8% of the potassium was left in the wood. Aluminum tended to be removed more slowly and even after 20 days only minor amounts of aluminum were removed from the wood. Total removal of alum was not obtained in the experiments reported here, but the high conductivity and the transport of the measured ions due to the electric field indicates that an applied electric field as a method for removal of alum and other unwanted ions from treated wooden objects warrants further investigation.

The use of an electric field for the removal of alum from treated wooden objects

In this paper the removal of sulfate and aluminum ions from waterlogged alum treated wood with the use of an applied electric field is in focus. Removal of alum is seen as the first step towards re-conservation of the wood with e.g. PEG. Alum treated wood samples from the Hjortspring finds (app. 350 BC) was used in this investigation and a total of six experiments are presented here. An electric DC field was applied across the wood for 4-20 days. A constant current of 1-5 mA was applied and the corresponding voltage drop initially low, often below 10 V. At the end of the experiments sulfate has moved as expected towards the positively charged electrode (anode) and after 20 days only 10% of the sulfate was left in the wood. The majority of the sulfate was removed with the use of the electric field. It was shown that it is possible to apply the electric field and remove sulfate in both experiments with and without presoaking. Aluminum tended to be removed more slowly and even after 20 days only minor amounts of aluminum was removed from the wood, The power consumption was low, only 1.6 Wh after 20 days. An increase in ph near the anode was found in some of the experiments. The reason is not obvious and further experiments are needed to evaluate the reason for this. Total removal of alum was not obtained in the experiments reported here, but the high conductivity and the transport of the measured ions due to the electric field indicates that an applied electric field as a method for removal of alum and other unwanted ions from treated objects should be further investigated. Research is ongoing and distribution of potassium after treatment will be measured in the near future.
Re-impregnation of wood with a Cu-anode

Utilization of electromigration in civil and environmental engineering - Processes, transport rates and matrix changes

Electromigration (movement of ions in an applied electric field) is utilized for supply or extraction of ions from various porous materials within both civil and environmental engineering. In civil engineering, most research has been conducted on the removal of chlorides from concrete to hinder reinforcement corrosion while in environmental engineering remediation of heavy metal polluted soil is the issue most studied. Never the less, experiments have been conducted with utilization for several other materials and purposes within both engineering fields. Even though there are many topics of common interest in the use of electromigration for the two fields, there is no tradition for collaboration. The present paper is a review with the aim of pointing out areas of shared interest. Focus is laid on the purposes of the different processes, transport rates of various ions in different materials and on changes in the matrix itself. Desorption and dissolution of the target elements into ionic form is a key issue to most of the processes, and can be the limiting step. The removal rate is generally below 1 cm day$^{-1}$, but it can be much less than 1 mm day$^{-1}$ when desorption is slow and insufficient. Matrix changes occurs under the action of the applied electric field and it includes both physico-chemical and hydrological changes. Some of the solid phases is weathered and new can be formed. Increased fundamental understanding of the effects and side effects, when applying the electric field to a porous material, can lead to improvement of the known technologies and possibly to new applications.

Publication Information
Volume: 43
Issue number: 8
ISSN (Print): 1093-4529
Ratings:
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 0.473 SNIP 0.459
Web of Science (2008): Indexed yes
Original language: English
DOIs:
10.1080/10934520801973949
Source: orbit
Source-ID: 222396
Utilization of electromigration in civil and environmental engineering

General information
Publication status: Published
Organisations: Department of Civil Engineering, Section for Construction Materials, Section for Geotechnics and Geology
Contributors: Ottosen, L. M., Christensen, I. V., Rörig-Dalgaard, I., Jensen, P. E.
Publication date: 2007
Peer-reviewed: Yes
Source: orbit
Source-ID: 207467

Electrodialytic remediation of CCA-treated waste wood in a 2 m³ pilot plant
Waste wood that has been treated with chromated-copper-arsenate (CCA) poses a potential environmental problem due to the content of copper, chromium and arsenic. A pilot plant for electrodialytic remediation of up to 2 m³ wood has been designed and tested and the results are presented here. Several process parameters were investigated, and it was found that the use of collecting units and soaking of the wood prior to the electrodialytic process had a positive influence on the remediation process. There was a tendency towards higher removal of CCA from wood chips <2 cm, compared to larger wood size fractions. The best remediation efficiency was obtained in an experiment with an electrode distance of 60 cm, and 100 kg wood chips. In this experiment 87% copper, 81% chromium and > 95% arsenic were removed. One other experiment was also analysed for arsenic. In this experiment the distance between the working electrodes was 1.5 m and here 95% As was removed. The results showed that arsenic may be the easiest removable of the copper, chromium and arsenic investigated here. This is very encouraging since arsenic is the CCA components of most environmental concern.

General information
Publication status: Published
Organisations: Section for Construction Materials, Department of Civil Engineering, NOVA University Lisbon
Contributors: Christensen, I. V., Pedersen, A. J., Ottosen, L. M., Ribeiro, A.
Pages: 45-54
Publication date: 2006
Peer-reviewed: Yes

Publication information
Journal: Science of the Total Environment
Volume: 364
Issue number: 1-3
ISSN (Print): 0048-9697
Ratings:
Scopus rating (2006): SJR 1.512 SNIP 1.581
Web of Science (2006): Indexed yes
Original language: English
Keywords: Pilot plant, Electrodialytic remediation, CCA-treated waste wood, Phosphoric acid, Oxalic acid
DOIs: 10.1016/j.scitotenv.2005.11.018
Source: orbit
Source-ID: 189803

Electrodialytic remediation of CCA-treated wood and residues from thermal treatment

General information
Publication status: Published
Organisations: Section for Construction Materials, Department of Civil Engineering
Contributors: Christensen, I. V., Ottosen, L. M., Pedersen, A. J.
Number of pages: 501
Pages: 427-445
Publication date: 2006

Host publication information
Characterization of residues from thermal treatment of treated wood and extraction of Cu, Cr, As and Zn

Thermal treatment of chromated copper arsenate (CCA) impregnated waste wood is a way to utilize the energy resource of the wood and at the same time to reduce the volume of the waste. An issue of concern in relation to the thermal treatment is As emission to the air. Meanwhile, there is still a matter to cope with when methods to avoid As emission are implemented: the residues with increased concentrations of Cu, Cr and As. In the present paper two different residues after thermal treatment are characterized: a mixed bottom and fly ash from combustion of CCA impregnated wood, and a charcoal from pyrolysis of treated waste wood. By SEM/EDX it was seen that the charcoal still showed wood structure with both tracheids and rays and that Cu, Cr and As were found inside this wood structure. Cu was found alone while Cr and As were often found together. By chemical analysis it was found, too, that the charcoal contained a high concentration of Zn, probably from paint. Chemical extraction experiments in HNO were conducted with the charcoal and it was found that the order of extraction (in percentage) was Zn > Cu > As > Cr. A SEM/EDX investigation of the mixed ash from combustion showed the presence of small particles with wood structure with elevated Cu and Cr concentrations, but most particles were irregular shaped matrix particles rich in Si, Al and K. Cr was abundant in many different particles including the lignin skeleton of the small, unburned wood pieces, but also inside silica-based matrix particles. Ca was often found associated with char-like (porous) particles, indicating that Ca-arsenates had been formed during combustion. Cu was often associated with Cr in the unburned wood pieces, whereas it was less abundant inside the silica-based matrix particles. Cu was also found in an almost pure form in a small layer on the surface of some matrix particles indicating condensation of volatile Cu species. Chemical extraction with inorganic acids showed the order of percentages mobilized as: As > Cu > Cr.

General information
Publication status: Published
Organisations: Section for Building Materials and Geotechnics, Department of Civil Engineering
Contributors: Ottosen, L. M., Pedersen, A. J., Christensen, I. V.
Pages: 87-98
Publication date: 2005
Peer-reviewed: Yes

Determination of the distribution of copper and chromium in partly remediated CCA-treated pine wood using SEM and EDX analyses
Soaking in different acids and electrodialytic remediation (EDR) were applied for removing copper and chromium from freshly Chromated Copper Arsenate (CCA) impregnated EN 113 pine wood samples. After remedial treatments, AAS analyses revealed that the concentration of copper (Cu) and chromium (Cr) could be reduced to a large extent. Scanning electron microscopy with simultaneous electron dispersive X-ray analysis (SEM/EDX) clearly demonstrated a distinct difference in the distribution of Cu and Cr due to experimental conditions. Before soaking, the Cu and Cr was mainly located in the cell wall. After soaking, a small amount of Cu and Cr was still present in the cell walls but larger particles were now found on wall surfaces. Most effective removal of Cu was obtained after soaking in phosphoric and oxalic acid followed by EDR; here numerous rice grain-shaped particles were observed containing large amounts of Cu and no Cr. Cr was most effectively removed after soaking in oxalic acid and subsequent EDR treatment or dual soaking in phosphoric acid and oxalic acid with and without subsequent EDR.
Electrodialytic remediation of CCA treated waste wood in pilot scale

When CCA (Chromated Copper Arsenate) treated wood is removed from service and turns into waste, the contents of Cu, Cr and As is still high due to the strong fixation of CCA in the wood. This high content of toxic compounds presents a disposal challenge. Incineration of CCA treated waste wood is not allowed in Denmark, instead the wood is to be land filled until new methods for handling the wood are available. Since the amounts of CCA treated wood being removed from service is expected to increase in the years to come, the need of finding alternative handling methods is very relevant. In this present study the utility of the method Electrodialytic Remediation was demonstrated for handling of CCA treated waste wood in pilot scale. The electrodialytic remediation method, which uses a low level DC current as the cleaning agent, combines electrokinetic movement of ions in the wood matrix with the principles of electrodialysis. It has previously been shown that it is possible to remove Cu, Cr and As from CCA treated wood using electrodialytic remediation in laboratory scale (Ribeiro et al., 2000; Kristensen et al., 2003), but until now, the method had not been studied in larger scale. The pilot scale plant used in this study was designed to contain up to 2 m³ wood chips. Six remediation experiments were carried out. In these experiments, the process was up-scaled stepwise by increasing the distance between the electrodes from initially 60 cm to finally 150 cm. The remediation time was varied between 11 and 21 days, and phosphoric acid and/or oxalic acid was used to facilitate the desorption of CCA from the wood. In the most successful of the experiments carried out, the concentration of CCA in the wood was reduced by up to 82 % for Cr, 88 % for Cu and at least 96 % for As.

Electrodialytic remediation of heavy metal polluted soil

When CCA (Chromated Copper Arsenate) treated wood is removed from service and turns into waste, the contents of Cu, Cr and As is still high due to the strong fixation of CCA in the wood. This high content of toxic compounds presents a disposal challenge. Incineration of CCA treated waste wood is not allowed in Denmark, instead the wood is to be land filled until new methods for handling the wood are available. Since the amounts of CCA treated wood being removed from service is expected to increase in the years to come, the need of finding alternative handling methods is very relevant. In this present study the utility of the method Electrodialytic Remediation was demonstrated for handling of CCA treated waste wood in pilot scale. The electrodialytic remediation method, which uses a low level DC current as the cleaning agent, combines electrokinetic movement of ions in the wood matrix with the principles of electrodialysis. It has previously been shown that it is possible to remove Cu, Cr and As from CCA treated wood using electrodialytic remediation in laboratory scale (Ribeiro et al., 2000; Kristensen et al., 2003), but until now, the method had not been studied in larger scale. The pilot scale plant used in this study was designed to contain up to 2 m³ wood chips. Six remediation experiments were carried out. In these experiments, the process was up-scaled stepwise by increasing the distance between the electrodes from initially 60 cm to finally 150 cm. The remediation time was varied between 11 and 21 days, and phosphoric acid and/or oxalic acid was used to facilitate the desorption of CCA from the wood. In the most successful of the experiments carried out, the concentration of CCA in the wood was reduced by up to 82 % for Cr, 88 % for Cu and at least 96 % for As.
Electrodialytic Removal of Cu, Cr and As from Treated Wood

The service life of wood treated with CCA (chromated copper arsenate) may be 20 years or more due to the strong fixation of CCA in the wood. This has lead to an extensive use of CCA-treated wood worldwide. The strong fixation however also means that a large proportion of the copper (Cu), chromium (Cr) and arsenic (As) is still present in the wood when it is removed from service and turns into waste. The content of As makes it a hazardous waste in many countries, including Denmark. The amount of impregnated waste wood is expected to increase dramatically and in Denmark alone it has been estimated that the amount of impregnated wood to be removed from service would increase from 17,000 tons in 1992 to 100,000 tons a year by 2010.

The aim of this thesis is to develop and optimise the Electrodialytic remediation (EDR) method to remediation of CCA-treated waste wood. The experiences obtained in this process are in the final part of the thesis discussed in the light of expanding the EDR method to other waste fractions.

Electrodialytic remediation (EDR) was originally developed for the removal of heavy metals from soil. The main principle behind EDR is that ions (including heavy metal ions) will move in an electric field and thereby be removed from the polluted material into liquids from where they can be collected. EDR uses a low voltage direct current as a cleaning agent and combines it with the use of ion exchange membranes to separate the electrodes from the polluted material (e.g. soil).

In this thesis the polluted material is CCA-treated wood in the form of wood chips. An additive was used in order to facilitate the removal process and it was found to be most beneficial to soak the wood in the additive prior to EDR as opposed to using the additive directly in the EDR setup.

The fixation of CCA in wood during impregnation is a complex and not fully understood process. However in the found literature there is an agreement on the fact that the reduction of Cr(VI) to Cr(III) is the driving force of CCA fixation in wood. Cr oxidise sites in the wood that may serve as strong fixation sites for the fixation products. Cu is mainly expected to be fixed independent of As and Cr. As is proposed fixed mainly as chromium arsenate and the remaining Cr is proposed precipitated as chromium hydroxide.

In Denmark the softwood species Norway spruce and Scots pine are the most used for wood preservation. The structure of softwood is fairly simple compared to hardwood. Softwood consist of 90-95% tracheids, 5-10% rays and 0.1-1 % resin canals.

In the found literature CCA is generally found to be distributed in all parts of the wood. There is a clear tendency to higher concentrations of CCA in the ray cells compared to the tracheids. This is in agreement with rays being the main penetration pathway for CCA.

Studies from the literature show that part of the CCA is leached from the wood during the service life but the use of a more balanced CCA formulation and the use of water repellent have decreased leaching during use. In general Cr was found to be the most leach resistant of the CCA-components. Several investigations have been made on the subject of actively extracting the CCA from the wood, in order to solve the increasing waste problem. CCA was reported to be removed to a large extend by different acids and complexing agents. Biological extraction by fungi and metal tolerant bacteria was also
able to remove CCA.

In the experimental work done in this thesis, wood from a CCA-treated out of service pole and a mix of impregnated waste wood was used.

The optimization of the Electrodialytic remediation method in laboratory scale was primarily focused on identifying the most suitable additive for the removal of Cu and Cr since these metals seemed to be more difficult to remove than As. Remediation at high pH was not successful, presumably due to precipitation of Cr and Cu at alkaline pH. It was not possible to locate one additive that was ideal for removal of both Cu and Cr. In an acid environment it was found that the most suitable additive for Cr was oxalic acid, whereas phosphoric acid proved to be best suited for the removal of Cu. Prior to EDR the wood was soaked in the two additives.

In the laboratory scale it was possible to remove 92% Cu and 83% Cr from a batch of 70 g wood and the average residual concentrations in the wood was 102 ppm Cu and 232 ppm Cr.

SEM analyses of partly remediated wood showed no indications of a specific CCAwood bonding that was not influenced by EDR. After soaking Cu and Cr was found to be present partly as precipitates on the lumen surfaces of the wood. After EDR the appearance seemed to be reduced in both tracheids and rays.

The EDR process was subsequently upscaled to a pilot scale that could remediate 0.3 – 2 m3 wood at a time by varying the distance between the electrodes. In an experiment with approximately 100 kg wood the removal efficiency was as good as in the laboratory. The final concentrations in the wood was 163 ppm Cu, 252 ppm Cr and less than 43 ppm As. Further upscaling resulted in reduced removal of Cu and Cr, but in the only other experiment that was analysed for As approximately 250 kg wood chips was remediated and the final concentration of As was less than 33 ppm. There was a clear tendency of decreased removal of CCA with increasing wood size fraction and increasing distance between the electrodes but at least the influence by distance is supposed to be diminished by the use of a stronger power supply.

Investigations in the laboratory showed that the presence of minor amounts of metallic metal pieces (like iron nails and copper wire) in the wood chip batches did not influence the remediation process significantly and makes the chipping and sorting of waste wood possible by commercial methods (shredding and magnetic separation of metallic metal pieces). This is very encouraging if EDR is to be used in larger scale.

The usability of the wood after remediation was investigated. If the wood is to be reused after the removal of CCA, the influence of oxalic acid on the strength of the wood may be important. Investigations of the influence of oxalic acid on bending strength of pine wood revealed no significant difference in the bending strength due to oxalic acid or EDR.

The process liquids from EDR were investigated for the direct use in impregnating new wood by CCA. The results showed that pre-treatment of the liquids were necessary before they could be reused.

The results and experiences that was gained in the optimization process, both in the laboratory and in the process of up scaling EDR to pilot scale may be used in the evaluation of other materials to be remediated with EDR. The most important characteristics of the polluted material is that the pollutant is to be present as ions in order to be removed by EDR. Identifying a suitable additive for the removal of the pollutants seems to be a key parameter and should be optimized with respect to concentration and pH, this may be done mostly by extraction experiments, but EDR experiments are needed in order to verify the suitability of the additive. Through EDR experiments the current density, optimum duration of the experiments, liquid to solid ratio are to be investigated. After optimising the EDR process in the laboratory, the up scaling may begin. In the large scale parameters including electrode distance, the use of collecting units and the membrane area are to be investigated. If the up scaling was successful, further up scaling to eventually industrial scale is possible.

In the case of CCA-treated wood, the up scaling of EDR to pilot scale was very promising. It was possible to remove almost all As which is the CCA component of most concern. The concentration of Cu and Cr was reduced to less than half of the initial concentration and further reduction can most likely be achieved with the use of a stronger power supply.

General information
Publication status: Published
Organisations: Section for Construction Materials, Department of Civil Engineering
Contributors: Christensen, I. V.
Number of pages: 182
Publication date: Oct 2004

Publication information
Place of publication: Kgs. Lyngby, Denmark
Publisher: Technical University of Denmark (DTU)
Original language: English
(ByG-Rapport; No. R-185).
Electrodialytic Removal of Heavy Metals from Different Solid Waste Products

A variety of heavy metal polluted waste products must be handled today. Electrochemical methods have been developed for remediation of polluted soil. One of the methods is the electrodialytic remediation method that is based on electromigration of heavy metal ions and ionic species within the soil matrix, and a separation of the soil and the process solutions, where the heavy metals are concentrated, with ion exchange membranes. For remediation of some soils, such as calcareous soils, it is necessary to add an enhancement solution. It was shown in a laboratory experiment that ammonium citrate could be used when removing Cu and Cr from a soil with 25% carbonates. The final concentrations of the elements were below the target values after the remediation. A question of whether the electrodialytic remediation method can be used for other waste products arose. Preliminary experiments showed that the method could be used for removal of different heavy metals from impregnated wood waste, fly ash from straw combustion, and fly ash from municipal solid waste incineration. The best result was obtained with the wood waste where more than 80% of each of the polluting elements Cu, Cr and As was removed in a 7-day experiment in which oxalic acid was used as enhancement solution. From the straw ash, 66% of the Cd was removed, but 64% of the fly ash dry mass dissolved during the treatment. In this actual experiment, no enhancement solution was used but that will be necessary to avoid dissolution of the ash to such a high extent. For the fly ash from waste incineration, ammonium citrate was tested as enhancement solution and in 14 days 62% Cd, 53% Cu, 6% Pb, and 31% Zn were removed. The preliminary results were thus promising for developing the electrodialytic method to other products than soil, although more research is needed especially in finding the best enhancement solutions for each product.
Electroosmotic dewatering of chalk sludge, iron hydroxide sludge, wet fly ash and biomass sludge

Electroosmotic dewatering has been tested in laboratory cells on four different porous materials: chalk sludge, iron hydroxide sludge, wet fly ash and biomass sludge from enzyme production. In all cases it was possible to remove water when passing electric DC current through the material. Casagrande's coefficients were determined for the four materials at different water contents. The experiments in this work showed that chalk could be dewatered from 40% to 79% DM (dry matter), fly ash from 75 to 82% DM, iron hydroxide sludge from 2.7 to 19% DM and biomass from 3 to 33% DM by electroosmosis. The process was not optimised indicating that higher dry matter contents could be achieved by electroosmosis. It was possible to relate Casagrande's coefficient directly to the electroosmotic coefficient obtained by dewatering experiments.

Removal of Arsenic from Toxic Ash after Combustion of Impregnate Wood

General information
Publication status: Published
Organisations: Section for Building Materials and Geotechnics, Department of Civil Engineering
Contributors: Ottosen, L. M., Pedersen, A. J., Christensen, I. V., Ribeiro, A.
Pages: 993-996
Publication date: 2003
Peer-reviewed: Yes
Electrodialytic remediation of heavy metal polluted soil: When is it optimal to use an electric current as cleaning agent?

General information
Publication status: Published
Organisations: Department of Geology and Geotechnical Engineering
Number of pages: 368
Publication date: 2000

Host publication information
Title of host publication: Book of Abstracts
Place of publication: Valencia, Spain
Source: orbit
Source-ID: 175757
Research output: Chapter in Book/Report/Conference proceeding – Annual report year: 2000 – Research

Electrodialytic soil remediation: Principle, changes in the soil system, and optimising the remediation process
The paper gives an overview of how heavy metals can be found in the soil and the theory of electrodialytic remediation. Basically electrodialytic remediation works by passing electric current through the soil, and the heavy metals in ionic form will carry some of the current. Ion-exchange membranes prevents the protons and the hydroxides ions from the electrode processes to enter the soil. The heavy metals are collected in a concentration compartment, which is separated from the soil by ion-exchange membranes. Examples from remediation experiments are shown, and it is demonstrated that it is possible to remEDIATE soil polluted with heavy metals be this method. When adding desorbing agents or complexing agents, choosing the right current density, electrolyte and membranes, the proces can be optimised for a given remediation situation. Also electroosmosis is influencing the system, and if extra water is not added, the soil can be dewatered because of this effect.

General information
Publication status: Published
Organisations: Department of Geology and Geotechnical Engineering, Department of Chemistry, New University of Lisbon
Pages: 81-89
Publication date: 1999

Host publication information
Title of host publication: Heavy Metals in the Environment and Electromigration Applied to Soil Remediation
Place of publication: Lyngby
Publisher: Technical University of Denmark, Environmental Electrochemistry
ISBN (Print): 87-987461-0-3
Source: orbit
Source-ID: 174128
Research output: Chapter in Book/Report/Conference proceeding – Annual report year: 1999 – Research

The effect of Soil Temperature on Electrodialytic Remediation

General information
Publication status: Published
Organisations: Department of Geology and Geotechnical Engineering
Contributors: Kristensen, I. V.
Pages: 92-98
Publication date: 1999

Host publication information
Title of host publication: Proceedings from: 2.nd Symposium on Heavy Metals in the Environment and Electromigration Applied to soil Remediation
Place of publication: Lyngby
Publisher: Technical University of Denmark, Environmental Electrochemistry