CHEMICAL PROCESS FOR EXTRACTING RESIDUAL PCP AND OIL CONCENTRATIONS FROM TREATED WOOD WASTES

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Abstract

A method has been developed for extracting chemical preservatives from pentachlorophenol-treated wood poles intended to be discarded. The average extraction yields obtained are 93% and 99.9% for the PCP and oil respectively. The process is fast and its mild chemistry does not lead to the formation of undesirable by-products. The main by-product consists of extracted wood fibre with an average PCP level of 610 mg/kg. Several patent applications have been filed and one patent has already been obtained from the United States (#5,262,004).

Résumé

Une méthode d'extraction de préservatifs chimiques du bois traité au PCP a été mise au point dans nos laboratoires. Cette méthode permet l'extraction de 93% du PCP et de plus de 99,9% de l'huile. Le procédé est rapide et sa chimie douce élimine la formation de sous-produits indésirables. Le sous-produit majeur est la fibre de bois qui contient en moyenne 610 mg/kg de PCP. Des demandes de brevets ont été déposées pour cette application et, à ce jour, un brevet nous a été octroyé par les États-Unis (#5,262,004).

1. Introduction

Pentachlorophenol (PCP) and its sodium salt (Na-PCP) are used as biocides throughout the world. The total installed volume of treated wood poles in Canada is estimated at 8,500,000 m^3 (Carroll-Hatch, 1994). The Québec power distribution system alone comprises 2.2 million poles, most of them treated with PCP, and every year approximately 80,000 new poles are added either for new lines or as replacements. A study conducted for Environment Canada in 1989 (Cooper and Ung, 1989) concluded that about 250,000 poles are discarded every year in this country, based on a total of 9 million poles installed with an average service life of 35 years. At Hydro-Québec, the average age of removed poles is estimated at 15 years and, until recently, the poles were reused or sold to the general public after removal. However, the demand for such poles is now decreasing and, even though federal and provincial regulations are still not too restrictive in this respect, pressure from environmental groups and the media is already forcing the utility to seek solutions that will be more acceptable, both economically and environmentally.

While evaluating the possibility of eliminating PCP by means of biological alternatives (Ottou, 1993), it was noticed that i) PCP in a wood matrix is not fully accessible to the microorganisms and ii) the microorganisms are extremely sensitive to high PCP concentrations, namely > 600 mg/kg. The residual PCP concentrations of in-service poles were found to be three to four times higher. These high concentrations are not necessarily detrimental, because of the limited accessibility of PCP to the microorganisms, but pretreatment of the wood is preferable in order to make all the PCP available and, also, to dilute it if necessary to below the lethal concentration for microorganisms.

A study was therefore undertaken to develop a chemical extraction process with a view to increasing the availability of PCP to microorganisms.

2. Methodology

The PCP and oil concentrations in the wood and water matrices were characterized using an analytical method developed at our lab (Besner *et al.*, 1994). This method allows the quantification of PCP by gas chromatography with an electron capture detector (GC-ECD) and of its petroleum solvent by Fourier transform infrared spectrometry (FTIR) from a single sample of soil, wood or water. Wood samples consist of 1-g amounts of finely ground borings, whereas liquid samples are volumes of 20 to 40 mL. The wood cores are sampled across the diameter of the pole using a 4.6-mm I.D. Pressler borer (Suunto, Finland) and the concentrations obtained are averages of the heartwood and sapwood areas.

A 40-ft Class 4 freshly treated red pine pole was chipped using an industrial shredder, Morbark model 27 RXL, and a certain amount of chips was further ground in a Retsch SM1 cutting mill (Brinkmann Instruments, Rexdale, Ont.) equipped with a 2-mm mesh bottom sieve to obtain a powder which was further homogenized using the four-quadrants method. This powder was used for conducting the extraction experiments.

The extraction of preservatives from the wood to give a final product which is non-toxic and free of preservatives is characterized by the following steps: i) wood chips are impregnated with an aqueous alkaline solution until softening and modification of the chemical state of the products to be extracted occur; ii) the wood chips are optionally cooked by pressurized steam and further exploded when the pressure is relieved; iii) the softened chips then undergo a crushing operation in a blender which shreds the wood, resulting in a substantial extraction of the preservatives; and iv) the PCP and the oil are collected separately from the particles of wood in the aqueous phases produced during impregnation, steaming-cooking and crushing.

Alkaline impregnation experiments were performed in conventional laboratory glassware. A small batch-mode reactor with a capacity of 75 g of wood chips was used to steam cook and explode the chips. The crushing was done with a Waring commercial blender, model 33BL34 (Waring Products division, New Hartford, Connecticut). The aqueous phases were filtered on a Whatman No. 4 paper filter. The extraction yields were obtained by measuring the PCP and oil concentrations in the wood samples before and after extraction.

3. Results and discussion

Residual PCP and oil of in-service poles. The PCP-treated poles installed on the Hydro-Québec distribution system have to meet the minimum retention of 6.4 kg/m^3 (*ca.* 12,800 mg/kg) of PCP in the sapwood as specified in CSA standards (CSA, 1989). The oil is not covered by a specific standard but is generally between 25 and 200 kg/m^3 (*ca.* 50,000 to 400,000 mg/kg) in sapwood (Besner *et al.*, 1991). These quantities decrease when the pole is put into service, as a result of different loss mechanisms. Figures 1 and 2 show the average concentrations of PCP and oil respectively across the full diameter of poles in service from 9 to 36 years as compared to freshly treated poles. It can be seen that half the poles still contain PCP and oil levels similar to those of freshly treated poles, indicating that either the losses are negligible or, more probably, the poles were initially treated with large amounts of preservative. Poles removed from service still contain substantial quantities of chemicals and their handling and disposal should remain the responsibility of the industrial users.

Chemical extraction. The initial conditions for optimization were as follows: 100 g of moist chips (75 g of dry wood) were impregnated with 225 g of a 4% weight solution of NaOH for 24 h at 60°C. This was followed by cooking the wood with steam at 195°C for 8 min and sudden decompression at atmospheric pressure, followed by crushing for 1.5 min with 2.5 L of water. The chips were subsequently washed with 2 L of water on a paper filter. The initial quantities of PCP and oil in the chips were 8,700 mg/kg and 99,000 mg/kg respectively on a dry matter basis, representative of the quantities found in a freshly treated pole, the worst case. At the end of the operation, there were 500 mg/kg of PCP and traces of oil for a yield of 94.6% for PCP and close to 100% for the oil. This PCP yield should be considered as minimal because impregnation at high pressure and use of an industrial shredder would improve the penetration of the alkaline solution in the cellulosic material and, hence, the shredding of the chips. The same experiment was repeated twice and gave extraction yields of 96.9 and 97.3% for the PCP and close to 100% for the oil, as seen in Table I.

The effect of the duration of the steam cooking step on extraction yields was evaluated and the results are presented in Table II. Reducing the cooking time from 8 to 0 min had little effect with the NaOH liquor, but lowered the yields when using water as a liquor or no impregnation at all. It is concluded that high extraction yields were obtained with a process including an impregnation step or a steam-cooking step and that little advantage (3-5%) was gained when both were used. Considering the complex setup used for the latter, it was dropped in favor of impregnation.

The NaOH concentration was lowered from 4 to 1% without affecting the extraction yields, as seen in Table III. The extraction yields obtained using water or a 0.1% NaOH were 10% lower for PCP. With a 4% NaOH liquor, the duration of the impregnation step was reduced from 24 to 1 h without affecting the extraction yields, as seen in Table IV. For a 1-h impregnation step using a 4% NaOH liquor, the temperature was lowered from 60 to 20°C. The average yields obtained for three replicates are respectively 92.5% and >99.9% for PCP and oil. This experimental condition produced wood fibres containing low PCP concentrations (500 mg/kg). Slightly lower concentrations, in the 200 mg/kg range, were obtained using the steam cooking step.

The optimal laboratory conditions of the process were set as follows. The impregnation was done for 1 h at ambient temperature and the steaming-cooking step was eliminated, as it only improved the extraction yields by 2 to 3%. The concentration of NaOH in the impregnation liquor could be varied between 0 and 1%, depending on the residual concentrations required by the secondary use considered. The crushing and separation steps remained unchanged. The average PCP and oil residual concentrations are respectively 610 and 100 mg/kg, the latter value being an estimate, since the oil in the wood fibre is undetectable after the extraction process.

PCP-treated wood samples were subjected to a Toxicity Characteristic Leaching Procedure (TCLP) to ensure they met the requirement of 2 mg/L for total phenols. The samples were analyzed by an independent laboratory approved by the Québec Environment Ministry (MENVIQ). The extraction process was applied to the wood powder and chips. The results are presented in Table V. The blank sample has a concentration of PCP lower than 0.002 mg/L, because of the clean glassware used. Surprisingly, every sample met the 2 mg/L requirement, even the unextracted chips ground to powder, which presents the largest surface area per mass unit and a high PCP content. The acidic pH of the leaching solution does not favor PCP solubility and the test is not adequate for this type of chemical. The characterization of PCP and oil concentrations in the total matter would be more appropriate, since the wood, as it degrades, could release larger quantities of these chemicals than those shown by the TCLP.

Elimination of by-products. The main by-products generated by the process are the wood fibres, which account for 90% of the total, the alkaline liquors containing the extracted PCP and oil, and the sludges. It appears to be almost impossible to reuse the sludges, which have to be incinerated. The alkaline liquors could be acidified and partitioned with oil to extract the PCP. This PCP-in-oil solution could be reused if treaters are interested. Wood fibres are less attractive than virgin chips because: i) aging modifies their homogeneity and ii) they still contain between 240 to 1,640 ppm (mg/kg) of PCP. For reuse, the wood must contain less than 0.01 mg/kg of PCP but such a low concentration calls for substantial efforts. Treated wood cannot be used for fuel in open fires under the Environment Protection Act. Burning wood fibres as fuel in a co-generator unit is an interesting avenue (Stalker, 1993) since the quality of the fibre has a minor effect, if any, on the combustion process, and the combustion would not be affected by the presence of PCP.

Like other processes, the chemical extraction generates by-products that can be either reused, recycled or eliminated. A combination of different processes is therefore necessary for the total management of waste and only an economic study can determine which processes to combine.

Disposal methods. The disposal methods for spent utility poles are presented in Table VI. Landfilling is still allowed in Canada but it will become increasingly unacceptable due to lack of space and the desire to recover the wood fibre. Bioremediation processes represent an interesting avenue to eliminate the residual PCP in wood, provided the PCP is accessible. This is perhaps not a viable option for a wood matrix, which needs a preceding extraction step to make the PCP accessible for the microorganisms. Biodegradation must therefore be seen as a polishing process after a chemical extraction step (Portier and Kressbach, 1992), but it is slow and it destroys the wood fibre. Two other methods have been proposed recently, namely thermolysis (Fransham, 1994) and burning PCP-treated wood waste in a cement kiln (Bernardin, 1994) without any treatment or chemical extraction. The former option could possibly lead to the formation of undesirable by-products while the latter option would first have to pass public hearings. The chemical extraction process is therefore an interesting alternative, and offers the appropriate versatility for eventually processing CCA-treated wastes.

Except for landfilling, all other processes need to be refined before they can handle large quantities of wastes. Meanwhile, users will have to stockpile their spent poles.

Towards a Canadian solution. The solution to the PCP-treated wastes problem can be summarized in four basic actions: extend the life of the pole by improving the management practices, so as to discard the strict minimum; process the strict minimum of the waste, by peeling the pole and saving the untreated centre core for further reuse; minimize the production of undesirable by-products and, finally, maximize the coordination, for logistical considerations (transportation, etc.), but also, hopefully, to pool all ideas circulating in Canada to find a solution for PCP-treated wood wastes.

4. Conclusion

A chemical extraction process has been developed that reduces the residual concentrations of PCP and oil in the wood to the hundreds of ppm level. Several patent applications have been filed and one patent has already been granted by the United States (#5,262,004). The process allows for the reuse of the wood fibre and does not lead to the formation of undesirable chemical by-products. The by-products generated by the chemical extraction have to be directed to secondary processes. An economic study will be needed to determine the best combination of processes.

5. Acknowledgments

The authors thank the Vice-présidence Environnement and Direction Planification et Valorisation de la technologie of Hydro-Québec for funding this project.

6. Literature

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Table I. Extraction yields at initial conditions

Impregnation					Extraction yield (%)	
Liquor	Duration (h)	Temperature (°C)	Steaming-cooking at 195°C (min)	Crushing (1.5 min)	PCP	Oil
4% NaOH	24	60	8	yes	94.6	>99.9
4% NaOH	24	60	8	yes	96.9	>99.9
4% NaOH	24	60	8	yes	97.3	>99.9

Table II. Effect of cooking time on extraction yields

Impregnation					Extraction yield[1] (%)	
Liquor	Duration (h)	Temperature (°C)	Steaming-cooking at 195°C (min)	Crushing (1.5 min)	PCP (RSD)	Oil
4% NaOH	24	60	8	yes	96.3 (1.2)	>99.9
4% NaOH	24	60	4	yes	96.6	>99.9
4% NaOH	24	60	0	yes	91.2 (1.4)	>99.9
Water	24	60	8	yes	84.3	>99.9
Water	24	60	4	yes	72.3	>99.9
Water	24	60	0	yes	79.6	86.2
No liquor	0	---	8	yes	81.1	>99.9
No liquor	0	---	0	yes	10.6	42.9

(1) Average of three replicates

Table III. Effect of [NaOH] on extraction yields

Impregnation					Extraction yield[1] (%)	
Liquor	Duration (h)	Temperature (°C)	Steaming-cooking at 195°C (min)	Crushing (1.5 min)	PCP (RSD)	Oil
4% NaOH	24	60	0	yes	91.2 (1.4)	>99.9
1% NaOH	24	60	0	yes	93.1 (1.3)	>99.9
0.1% NaOH	24	60	0	yes	81.7 (0.7)	>99.9
0 % NaOH	24	60	0	yes	79.6	86.2

[1] Average of three replicates

Table IV. Effect of impregnation time on extraction yields

Impregnation					Extraction yield[1] (%)	
Liquor	Duration (h)	Temperature (°C)	Steaming-cooking at 195°C (min)	Crushing (1.5 min)	PCP (RSD)	Oil
4% NaOH	24	60	0	yes	91.2 (1.4)	>99.9
4% NaOH	12	60	0	yes	94.2 (0.7)	>99.9
4% NaOH	6	60	0	yes	92.8 (2.2)	>99.9
4% NaOH	1	60	0	yes	92.6 (1.6)	>99.9

[1] Average of three replicates

Table V. Toxicity characteristics of PCP-treated wood leachates

Sample	[PCP] in wood (mg/kg)	[PCP] in leachate (mg/L)
Blank	---	< 0.002
Extracted Chips #1	590	0.710
Extracted Chips #2	800	0.600
Extracted Chips #3	500	0.650
Unextracted chips⁽¹⁾	8,700	0.750

(1) Reduced to powder

Table VI. Disposal methods for spent utility poles

Method	
In-situ landfilling	To be banned in a near future
Controlled landfilling	Small quantities
Biotreatment	Long, seasonal Clean Stand-alone process (?) Acceptance from the public
Incineration	Recycling as fuel Controlled conditions ($T \geq 1,200$ °C, $\tau_r \geq 2$ s, $O_2 = 3\%$) Subjected to public approval
Thermolysis	Fast Undesirable by-products (?)
Chemical extraction	Fast Mild conditions Versatility

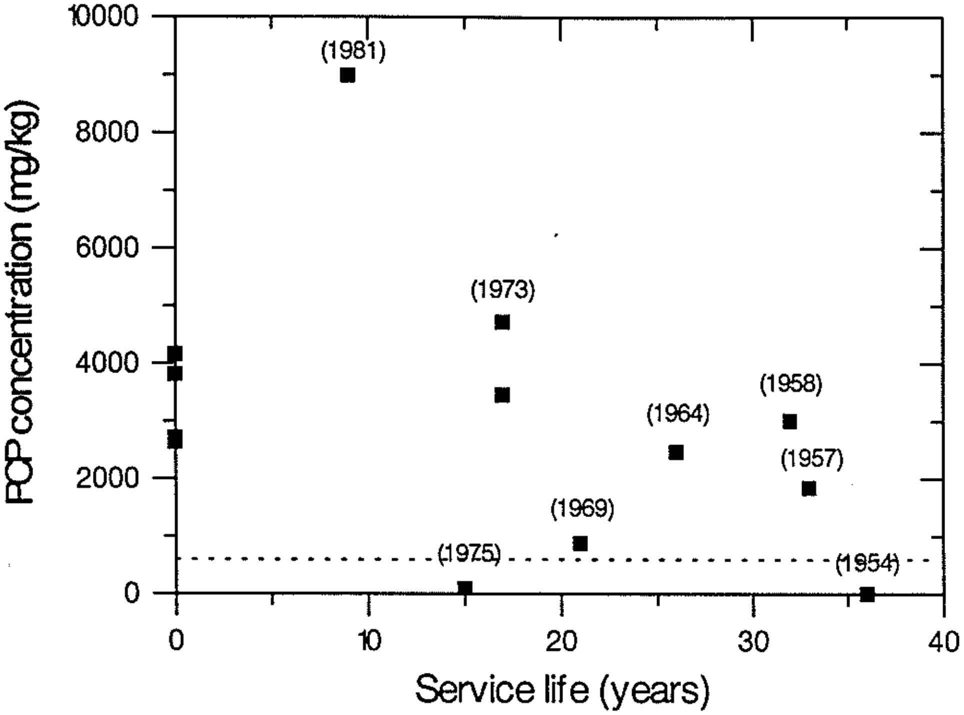

Figure 1. Residual PCP concentrations of in-service poles

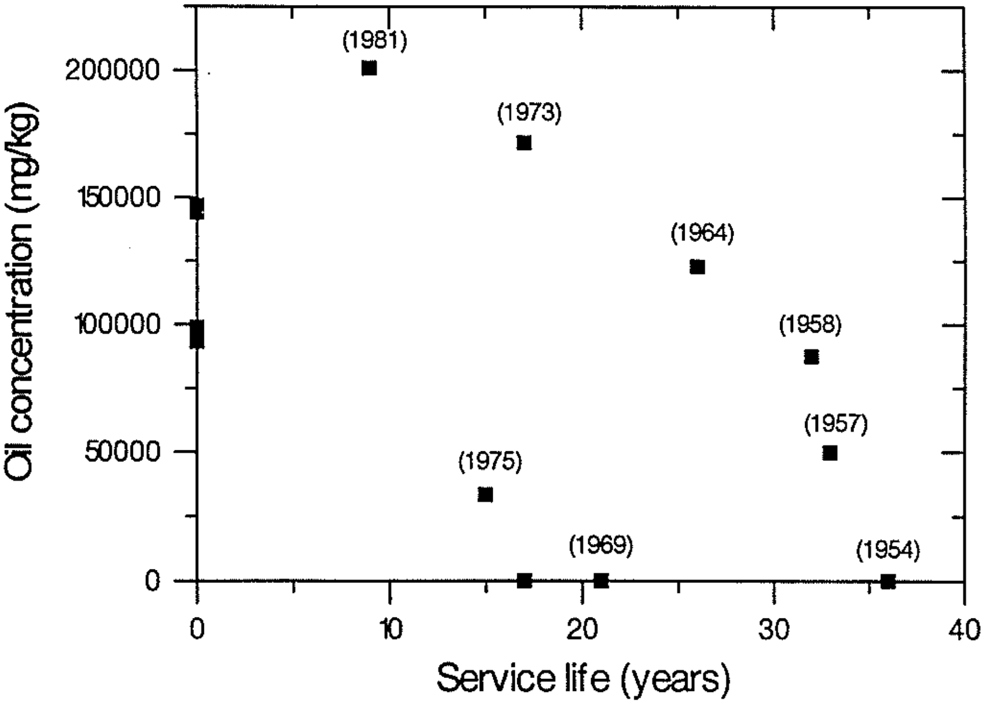

Figure 2. Residual oil concentrations of in-service poles