THE FORMATION OF CHROMIUM(V) DURING NORMAL AND ACCELERATED FIXATION OF CCA IN TREATED LUMBER.

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Summary

Western hemlock lumber treated with 1.2% CCA-C was subjected to normal fixation at ambient temperature (24 ± 4°C) or, accelerated steam fixation at 80°C for 4 hours followed by fixation at ambient temperatures. Match stick specimens removed from the treated lumber surface were analyzed using electron spin resonance (ESR) spectrometry to examine the reduction of chromium(VI) to chromium(V) and chromium(III) during fixation. A strong chromium(V) ESR signal appeared soon after the CCA treatment. It weakened gradually, diminishing to a trace signal during the normal 3 week fixation, while the accelerated fixation specimens did not exhibit the Cr(V) signal after steam fixation. The amount of CCA leached was much less in the accelerated fixation than from the normal fixation within 1 week after the CCA treatment, whereas there was no significant differences in the amount of CCA leached between the normal and the accelerated fixation, 3 weeks after the CCA treatment. Leachate did not contain Cr(V) and Cr(III) species.

1. Introduction

Understanding the fixation process of preservatives is an important point to develop better preservative systems, with respect to not only preservative permanence, but also to address environmental concerns. The influences of temperature and moisture on the fixation of chromated wood preservatives has been widely investigated by a number of authors, including McMahon *et al.*, 1942; Conradie and Pizzi, 1987; Peek and Willeitner, 1988; Cooper and Ung, 1989; Avramidis and Ruddick, 1989; Forsyth and Morrell, 1990; Peek and Klipp, 1990; and Sonobe *et al.*, 1991. The fixation mechanism of chromium based wood preservatives has been studied by means of chemical analysis of precipitate and leachate, or measuring pH-changes and electrical resistance (Dahlgren and Hartford, 1972; Pizzi, 1980, 1982 and 1990; Evans and Nossen, 1989; Cooper and Ung, 1989).

The fixation of chromated-copper-arsenate (CCA) is dependent on the conversion of soluble hexavalent chromium compounds to insoluble trivalent chromium complexes. The chemical reaction with wood proceeded via a chromium(V) intermediate to a chromium(III), which was studied using electron spin resonance spectroscopy (ESR) (Plackett *et al.*, 1987, Hughes et al., 1992, Yamamoto and Ruddick, 1992). The toxicological properties and leachability of this chromium(V) species are not known. Previous experiments using match stick specimens showed that the Cr(V) species persisted in normal fixation for a long period (Ruddick *et al.*,

1994) The objective of this study was to reveal the behaviour of the chromium(V) species in CCA-treated hemlock lumber, subjected to normal and accelerated fixation.

2. Materials and Methods

Western hemlock (*Tsuga heterophylla*) flat square lumber, 4.4 x 8.7 mm in dimension and 2 m in length was selected for study from a lumber company located near Tsukuba, Japan. The lumber were conditioned to 12% moisture content at ambient temperature for six months, and was cut into two end-matching samples for normal fixation and accelerated fixation experiments. The lumber was incised on all four faces, the incision density being 3,787 incision/m^2. Two stacks of 4 x 4 lumber for normal fixation and accelerated fixation were made and treated with a 1.2% solution of CCA type C (20°C) using the following pressure schedule - initial vacuum 60 kPa, 30 minutes; 1300 kPa pressure, 4 hours; final vacuum 60 kPa, 6 hours 30 minutes. Stickers were used only in the stack for the accelerated fixation experiment. The mean solution retentions were 499 kg/m3 in the stack using stickers and 480 kg/m3 in the stack without stickers. Immediately following the impregnation treatment, the former stack was subjected to steaming for accelerating the fixation of CCA. The steaming condition was 80 ± 2°C for 4 hours. The later stack was allowed to fix at ambient temperature (24 ± 4°C) in the laboratory.

The specimens for ESR, 2.0 mm in width, 1.7 mm in depth, and 45 mm in length were cut from the surface of lumber with a groove planer, at time intervals of 0, 1, 4, 7, 14, 21, 35, 70 days after the pressure treatment. The specimens after removal were stored immediately in a thermos flask cooled with dry ice and then kept in a freezer at -18°C for less than 1 week, before measuring their ESR spectra.

All ESR spectra were recorded at -30°C to reduce the dielectric loss in wet specimens, with a JEOL JES-RE1X X-band spectrometer. The typical experimental conditions were: microwave frequency, 9.225-9.231 GHz; power, 1 mW; scan time, 8 minutes.(2.0 kG scanning); time constant 0.1sec.; modulation, 1.0 G. chosen to be less than 1/6 of the ESR line width of Cr(V) signal. A frequency counter was used for calibration and Mn(II) in MgO was used as a reference standard.

The CCA-treated lumber allowed to fix under the normal condition for 3 weeks or steam fixed for 4 hours followed by storing in the normal condition for 3 weeks, were subjected to a leaching experiment following the European Standard test method (European Standard, 1979). Each of two selected lumber from the fixation systems were soaked with distilled water in stainless steel baths and allowed to stand for two weeks changing the water every three or four days. The match sticks removed from lumber which had been analyzed with ESR, were also subjected to the leaching test. The concentrations of chromium, copper, and arsenic in the leachate were determined by atomic absorption spectrometry.

3. Results and discussions

3.1 Time dependence of chromium reduction in normal fixation

CCA treated wood stored at ambient temperature contained both chromium(V) and chromium(III) species (Figures 1a to 1c). The ESR spectra of samples collected soon after completion of the CCA treatment, revealed a strong Cr(V) signal at $g = 1.980$, and a copper(II) signal with typical hyperfine splitting, which overlaid the broad Cr(III) signal which was being generated (Figure 1a). The Cr(V) signal reached its maximum height one day after the CCA treatment, and then weakened gradually with time. The Cr(V) signal was not detected 70 days after the CCA treatment. It must be noted that the Cr(III) signal being generated during fixation was superimposed on a stable Cu(II) signal at the early stages of fixation (Yamamoto and Ruddick, 1992). The ESR parameters of Cu(II) were $g_{//} = 2.395$, $A_{//} = 130\text{x}10^{-4}\text{cm}^{-1}$, $g = 2.081$. The magnitudes of $g_{//}$, g , and $A_{//}$ provide an insight as to the nature of the ligands in the Cu(II) complexes formed in the wood (Sakaguchi and Addison, 1979). The ESR parameters here are consistent with a $d_{x^2-y^2}$ ground state of Cu(II) complexed by ligands arranged in a square planer (distorted octahedral) environment about the central cation, and bounded to four (six) oxygen atoms which are either functional groups of the wood, or water molecules (Senesi *et al.*, 1989). The hyperfine splitting of Cu(II) became unclear with time, which may be caused by the increased magnitude of the Cr(III) signal (Figures 1b to 1d). It has been noted that CCA preservative treated wood gives poor quality copper ESR spectra, due to the close presence of Cr(III) ions which cause line broadening (Hughes *et al.*, 1992).

The Cr(III) signal centered at 3310 Gauss, with line width 530 Gauss, changed its appearance slightly during fixation. The Cr(III) signal 70 days after the CCA treatment became clearer and stronger compared with that observed 21 days after the treatment (Figures 1c and 1d). This indicated that the transformation of Cr(V) to Cr(III) progressed slowly at room temperature and may provide indirect evidence for the occurrence of Cr(IV) species as intermediate products. The detection of Cr(IV) is very difficult, but Cr(IV) intermediates may be produced during the reduction of Cr(V) compounds to those involving Cr(III) (Wiberg and Schafer, 1969, Wilkinson, 1987).

The changes of the Cr(V) signal heights with time are shown in Figure 2. The heights can not be compared directly, as the match stick specimens analyzed were not the identical with respect to the amounts of CCA chemicals impregnated and their wood structures (such as the ratio of earlywood and latewood). A strong Cr(V) signal was observed soon after the CCA treatment. Cooper and Ung (1989) have suggesated that the initial reduction of Cr(VI) to Cr(III) progresses during the pressure treating cycle. The Cr(V) signal reached a maximum height within one day at ambient temperature. And then the Cr(V) signal weakened gradually with time during the normal fixation. The Cr(V) signal was still detected as a trace, 21 or 35 days after the treatment, and disappeared within 70 days after the treatment. Contrary to this, the Cr(V) ESR peak was still detected after 6 months when laboratory specimens were treated and analysed (Hughes *et al.*, 1992, Yamamoto and Ruddick, 1992). Hughes *et al.* (1992) have concluded that the Cr(V) species is stable and unlikely to be an intermediate.

It is proposed from these studies, that the Cr(V) species persists for a long time under conditions where the wood moisture content is insufficiently high during all stages of fixation. Such conditions may occur in thin samples stored under laboratory conditions, where the dimension of the treated specimens is not large enough to keep the wood moisture sufficiently high during fixation unless precautions are taken to maintain the wood moisture content. McNamara(1989) demonstrated that chromium(VI) could not be detected at 14 days fixation, in the total chromium present in solutions squeezed from CCA treated southern yellow pine sapwood blocks, stored at 21.5°C in the dark. The fixation was 98% or greater, based upon analysis of the total chromium and chromium(VI) in the solution squeezed from the blocks. About 20 days were required for complete fixation in CCA-treated red pine poles maintained at room temperature (21°C) based on the Cr(VI) content in squeezed solution from poles (Cooper and Ung, 1989). Their results, based upon analyzing the presence of Cr(VI) using a chromotropic acid test, clearly demonstrated that the reduction of Cr(VI) was practically complete within two or three weeks in CCA treated wood storing at room temperature. This study, however, showed Cr(V) species persisted more than three weeks at room temperature and that the completion of Cr(VI) reduction to Cr(III) requires more than three weeks during normal fixation.

3.2 Time dependence of chromium reduction in accelerated fixation

The ESR spectra for CCA treated wood steamed at 80° for 4 hours contained only Cr(III) signal (Figures 3a to 3c). The specimens even immediately after the accelerated fixation, did not exhibit any Cr(V) signal at all (Figure 3a). No major differences in the ESR spectra occurred with time, after completion of the steam fixation (Figures 3a to 3c). In these experiments using lumber, the reduction of Cr(VI) to Cr(III) was completed during the accelerated steam fixation for 4 hours. This is consistent with previous ESR work using small specimens during which the Cr(V) signal disappeared during steaming for 2 hours (Ruddick *et al.* 1994). During steaming fixation, the reduction of Cr(VI) to Cr(V) appears to be rapid, and the generated Cr(V) intermediate, quickly reduced to Cr(III).

3.3 Leachability

The amounts of copper and chromium leached from specimens within four days of storing after CCA treatment, were much less after the accelerated steam fixation than following the normal fixation. Contrary to this, the loss of arsenic was greater from the samples recovered from lumber subjected to accelerated fixation (Table 1) The higher arsenic leachability during the early stages of fixation following accelerated fixation was unexpected, and contrasts to conclusions that arsenic is fixed more rapidly than copper and chromium (McMohen *et al.*, 1942, Cooper and Ung, 1989). Copper arsenate or chromium arsenates has been thought to be fixation products in CCA-treated wood (Dahlgren and Hartford, 1972; Pizzi, 1982; Mutandadzi and Evans, 1990; Kojima and Ishihara, 1990). It is possible that the copper arsenate or chromium arsenate fixation products may be interfered with by the rapid formation of chrome chromates or copper chromates during accelerated fixation. Hager (1969) has proposed that a slow hydrolysis of copper arsenate and chromium arsenate in treated wood in service generates a leachable arsenic compound. A similar hydrolysis reaction could take place during steaming of treated wood. Additional information is needed to confirm the formation of chrome chromates or copper chromates within wood.

With time, the difference between the amounts of CCA elements leached from the samples fixed using normal and accelerated processes became small, and disappeared by three weeks after the CCA treatment, in the matched timber (Table 2). All of the CCA elements were almost completely fixed to the wood during the normal fixation at ambient temperature for three weeks or the accelerated fixation for four hours.

The intensity of Cr(V) signal in match stick specimens decreased greatly during two weeks of leaching. However ESR spectra of the leachate did not show any Cr(V) or Cr(III) signals (Figures 4a to 4d). The leachate exhibited only a Cu(II) signal. This indicated that the Cr(V) and Cr(III) complexes were either unstable or insoluble in water. These observations support the monitoring chromium(VI) as the best practical method of monitoring the fixation process.

4. Conclusions

Electron spin resonance spectrometry (ESR) was an effective way to examine the reduction of chromium(VI) to Cr(V) and Cr(III) during the CCA fixation. A strong Cr(V) ESR signal observed in samples removed from hemlock lumber just after CCA treatment, disappeared during accelerated steam fixation. The Cr(V) signal persisted and diminished into the trace signal during the normal fixation for three or five weeks. Leachate did not contain either Cr(V) or Cr(V) species. More work on the investigation of intermediate Cr(V) complexes formed with wood or CCA elements is needed to give a more complete picture of CCA fixation.

Steaming CCA-treated wood, accelerated fixation of copper and chromium, but not arsenic. During accelerated fixation, the amount of copper and chromium leached was much less, and that of arsenic more, than the quantities removed in the early stages of normal fixation. It is possible that the formation of copper arsenates or chromium arsenates as fixation products may be interfered by rapidly produced-chrome chromates or copper chromates during accelerated fixation.

5. References

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Table 1 Change in the amount of CCA leached during two weeks of leaching from match stick specimens, with increasing time of fixation.

Amount of elements leached (μg)

Elements	Fixation Conditions	0	1	4	14	21
Copper	Normal	9.8	8.5	3.9	2.3	0.5
	Accelerated	0.7	0.5	0.7	0.3	0.6
Chromium	Normal	40.0	24.0	31.2	2.9	1.2
	Accelerated	1.5	1.0	1.3	1.2	1.1
Arsenic	Normal	9.5	8.4	6.6	13.8	33.9
	Accelerated	27.1	25.3	25.0	25.1	26.5

Table 2 Percent of chromium, copper, and arsenic leached from end matched timber after accelerated steam fixation and three weeks storage, and normal fixation for three weeks, using a leaching regime of two weeks.

Specimen	Chromium	Copper	Arsenic
Normal Fixation	0.28	0.45	1.10
Accelerated Fixation	0.27	0.41	1.11

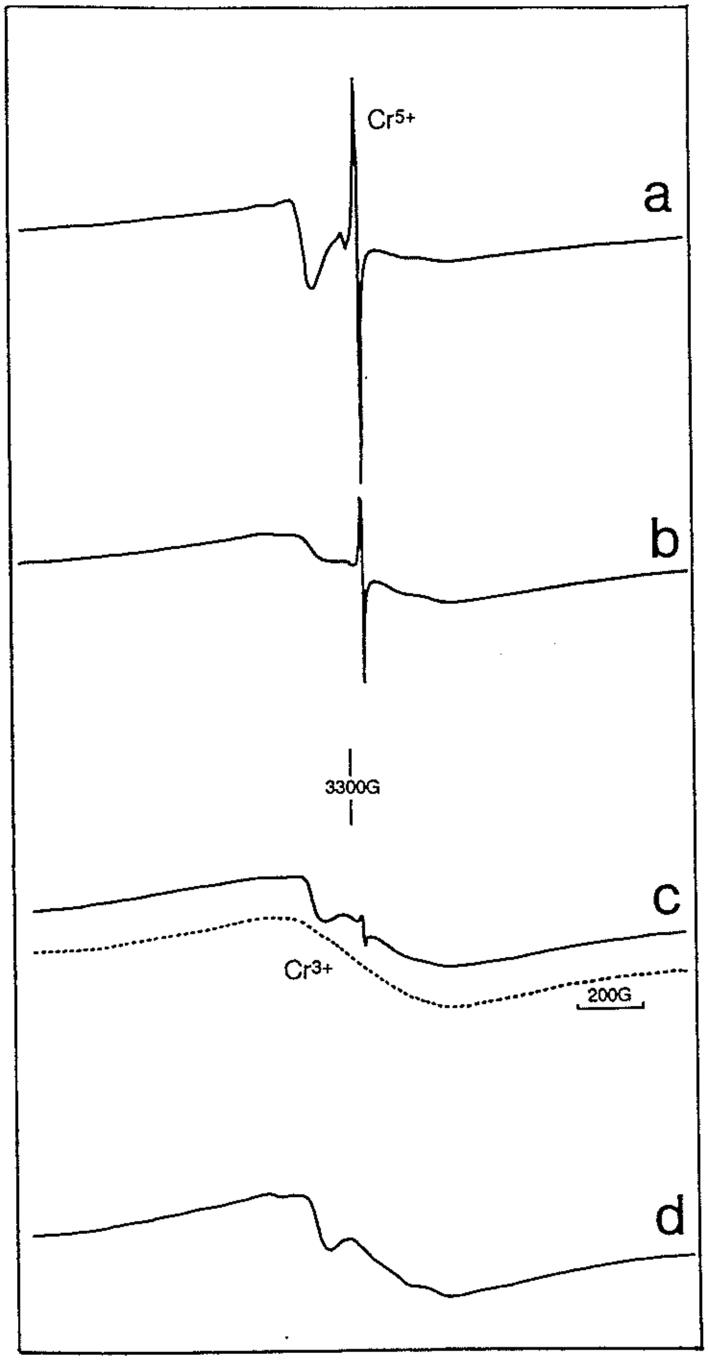

Fig. 1 ESR spectra showing time dependence of chromium(VI) reduction to chromium(V) and chromium(III) in CCA-treated western hemlock lumber, stored at ambient temperature. a: 0 day after the CCA treatment, b: 7 days after the CCA treatment, c: 21 days after the CCA treatment, d: 70 days after the CCA treatment.

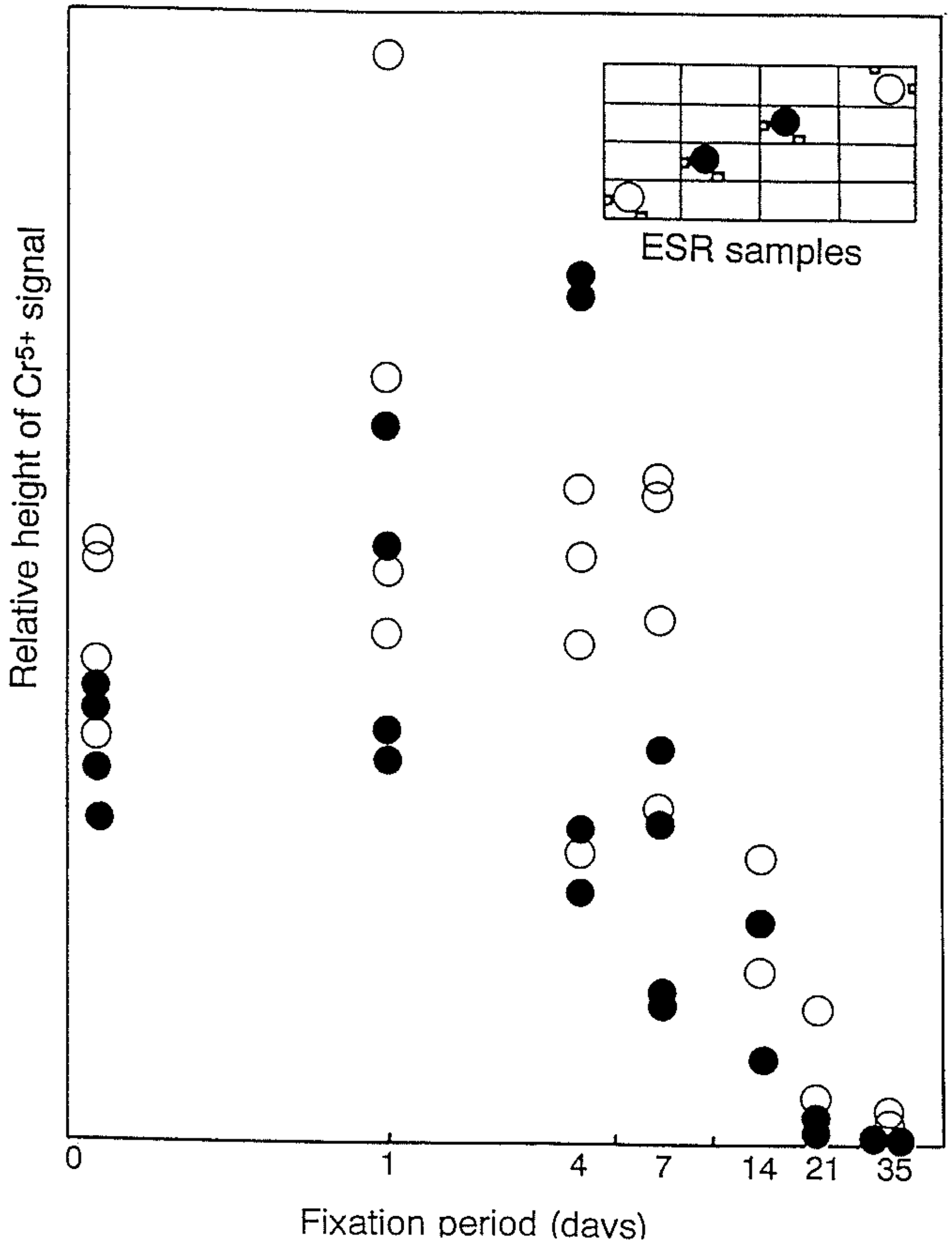

Fig. 2 Effect of fixation time on the height of the chromium(V) ESR signal generated match stick specimens taken from the outer (hollow circles) and inner (filled circles) CCA-treated western hemlock lumber lumber in stack.

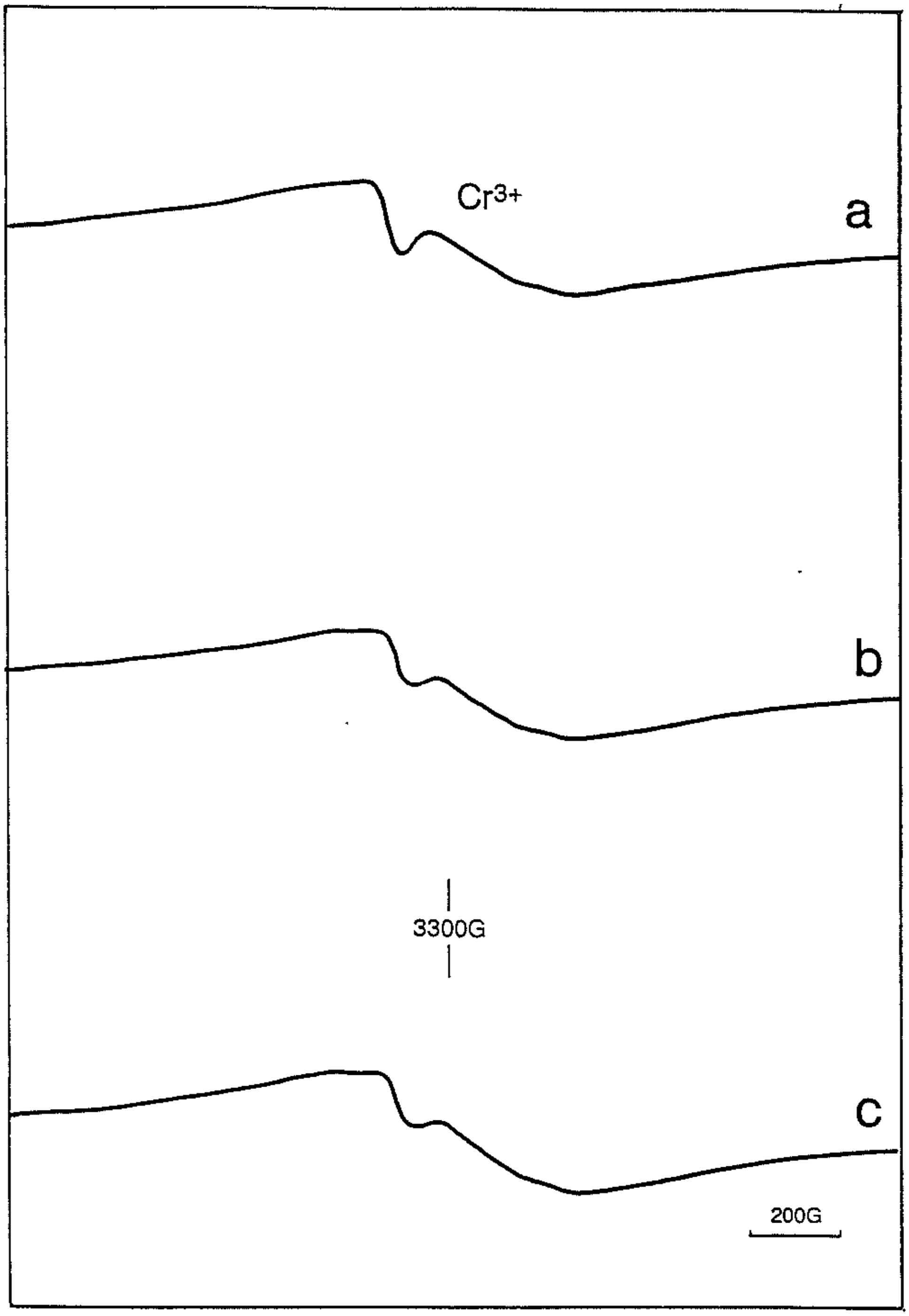

Fig. 3 ESR spectra showing time dependence of Cr(VI) reduction to Cr(III) in CCA-treated western hemlock lumber, after steam treatment at 80°C for 4 hours: a) soon after the steam treatment, b) 7days after the steam treatment, c) 21 days after the steam treatment.

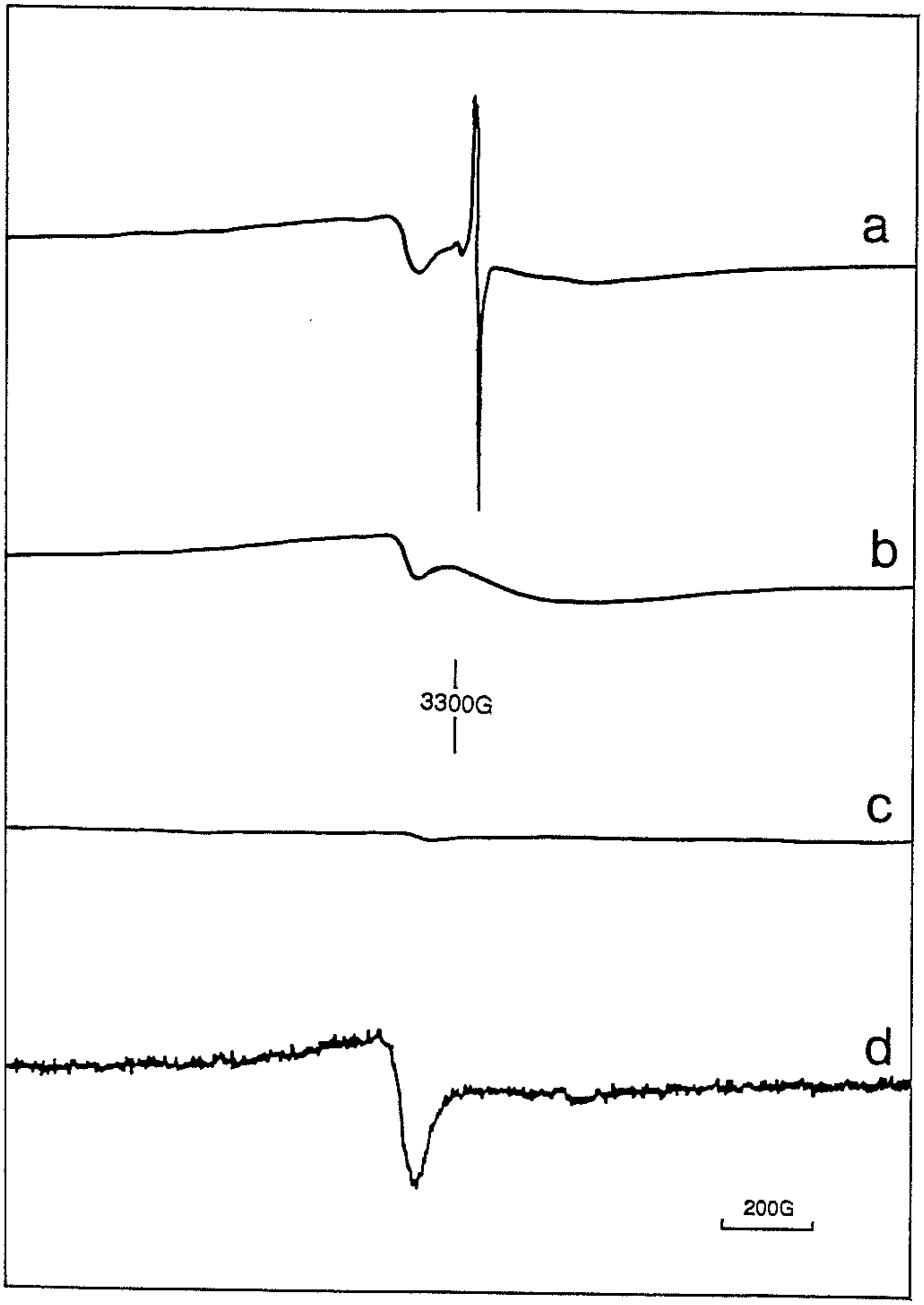

Fig. 4 Change in the Cr(V) signal during leaching. a: ESR spectrum of wood before leaching, b: ESR spectrum of wood after 2 weeks fixation 7 leaching, c: ESR spectrum of leachate, d: same as c, gain 20x.