THE ACCELERATED FIXATION OF CHROMATED COPPER PRESERVATIVE TREATED WOOD

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1. SUMMARY

Accelerated fixation of chromated copper preservatives is reviewed in this paper with respect to:-

- the chemical mechanism of fixation
- the physical and chemical factors which influence the rate of fixation
- the ways in which the key factors of influence may be brought in to play to accelerate fixation
- the practical considerations of equipment, relative cost and operability
- practical industrial scale applications of accelerated fixation

2. INTRODUCTION

When the soluble chemicals in CCA solutions react with wood components, insoluble reaction products are formed which protect wood for more than 40 years, even when subjected to severe leaching exposures. The term used by industry to define this condition whereby CCA chemicals become stable to leaching is referred to as fixation. The chemistry of this process has been extensively studied and it is now possible to review the complex reaction process as well as understand the more simple parameters which are of key concern to pressure treaters. In this paper the mechanism of fixation, the key parameters, and practical considerations likely to result in more rapid fixation are presented.

3. THE CHEMISTRY OF CCA IN WOOD

The course of fixation of CCA chemicals in wood has been studied by various authors (Refs 6-11, 19, 20, 29-32, 39, 40). These authors generally describe the reaction as occurring in three phases and the chemistry involved in each of these periods will be briefly discussed.

3.1 The period of momentary initial reaction

When dilute CCA solutions are injected into wood, they are instantly, or very rapidly, "chemically" absorbed on to cellulosic and lignin structures. Pizzi (Ref 29) estimates this momentary reaction rate in very dilute solutions by changes in the pH of the medium. The curves in Figure 1 show the very rapid pH increase when hexavalent chromium reacts with glucose during the absorption phase of the reaction, as long as glucose (a building block of cellulose) is in molar excess.

3.2 The period of primary precipitation fixation

While some of the hexavalent chromium remains fixed to the cellulosics and lignin by strong co-ordination bonds (chemical absorption) for extended periods of time, most of the chromium is reduced to the trivalent state during the primary precipitation fixation period. This redox reaction is expressed stoichiometrically as:

$$CrO_3 + 6H^+ + 3e \longrightarrow Cr^{+3} + 3H_2O$$

or as a model with D(+) glucose

$$4\ Cr_2O_7^{=} + C_6H_{12}O_6 + 32H^+ \longrightarrow 6CO_2 + 22H_2O + 8Cr^{+3}$$

Figure 2 shows the consensus of possible fixed products existing at the end of the primary precipitation fixation period and the final conversion according to Dahlgren et al (Refs 6-11).

It is possible, and probably likely, that the mixture of compounds which form can vary in type and in degree, depending on the condition of the treating solution and other variables. Nevertheless, the products formed always seem to provide the same predictable performance in wood.

3.3 The period of conversion reactions

The reaction products formed by the end of the primary fixation period are highly fixed. However, reactions continue for many weeks and perhaps months under certain exposure conditions. As the pH continues to rise at the end of the primary reaction period due to further reduction of the co-ordinated hexavalent chromium, copper arsenates undergo additional reactions to form the final basic copper arsenate product shown in Figure 3 (Ref 9). However an alternative reaction scenario is proposed by Pizzi - Figure 4 (Refs 29, 30, 31, 32) - which proposes some intermediates being formed before the final products of Dahlgren and Hartford.

Interestingly, the reaction of CCA with wood can be compared with the reaction of concrete components with reference to the three reaction patterns. They both have an initial reaction cycle and they both become highly fixed during their primary reaction period. Although concrete is "set" within a day or two, the conversion reaction continues for a couple of years.

3.4 Other considerations

Some recent work by Ostmeyer (Ref 19) using X-ray photo electron spectroscopy suggests that most of the reaction of chromated copper arsenate with wood may take place at the lignaceous sites and not to such a great extent in the cellulosic regions as implied by some earlier authors. The mechanism proposed was the formation of chromate esters at sp^2 and aromatic carbon sites (Figure 5). A mechanism was proposed for explaining the differences between CCA performance against softrot in softwoods and hardwoods. It was suggested that the lignins, which in conifers contain coniferyl alcohol and in hardwoods contains both coniferyl and sinapyl alcohols, because of their different composition offer greater opportunity in the case of softwoods for chromate ester formation and enhance fixation in softwoods over hardwoods. This mechanism is similar to that implied by Pizzi. A second area of work by the same authors (Ref 20) using Diffuse Reflectance Fourier Transform Infra-red spectroscopy (DRIFT) looked at solid treated timber. The joint conclusion with their earlier technique of XPS and were:-

(i) Substitution reactions on the aromatic rings of lignin allows formation of chromate esters.

(ii) Chromate esters remain as stable complexes without decomposition.

(iii) No evidence of oxidation of hydroxyl groups to carbonyls.

(iv) Reaction and bonding with other carbonyl groups in wood.

The work of Ostmeyer et all is interesting in suggesting alternative reaction scenarios in treated wood, it is unfortunate that it can only offer suggestions on chromium fixation and then only on Cr^{VI}. It does not offer any further light on Cr^{3+} or Cu^{2+} or $H_xAsO_4^{y-}$ fixation and as such its importance must be qualified. Additionally, proposals that imply chromium is substantially fixed as Cr^{VI}, seem to be at odds with most of the established data.

These ideas may however be very relevant in consideration of how CCA acts at the microscopic level to inhibit decay. For that reason the following summary suggestion is offered.

A possible composite theory which incorporates the work of Dahlgren, Hartford, Pizzi et al, Ostmeyer, Greaves and Levy (Ref 15) is that there are at least two modes of fixation which give rise to differing products and are essentially different in effect. These modes could be summed up as:-

(i) Macro fixation : Giving predominantly macroscopic inorganic reaction production deposition.

(ii) Micro location : Giving predominantly microscopic inorganic/organic products and complex deposition.

Of these two, by virtue of the rapid reaction between CCA, wood extractives and wood surfaces, probably in the more available fluid pathways within the wood structure, macro fixation is likely to be the predominant chemical "fixation" process. The latter micro location process and its products might however give rise to the fine variation in performance of CCA between species of treated wood by precise location of copper etc at sites where its activity might be most effective.

This differentiation between "fixation" and "location" is also encompassed within the work of Greaves and Levy where the micro distribution of CCA was investigated to explain softrot in hardwoods.

For the CCA treating industry considering the environmental impact of treating it is "macro fixation" which is the important factor and which is discussed in the following sections.

4. VARIABLES AFFECTING FIXATION

The laws which determine the reactions of CCA in wood are the same as those which affect standard chemical reactions. A list of variables, both major and minor, which affect this reaction are shown in Figure 6. It is extremely important to recognise that most of these variables can be controlled, indeed some of them must be controlled, to ensure adequate fixation before CCA treated wood is shipped from the plant.

4.1 Temperature

The rate at which a reaction takes place is a function of temperature. The specific reaction rate is related to the thermochemical properties of the reaction by the Arrhenius equation (Figure 7) which enables the energy needed to bring about reaction to be brought into consideration. This approach shows with many reactions which occur at reasonable rates at ambient temperatures that the specific reaction rate increases rapidly with temperature often in the range of 1 to 3 times per 10°C rise in temperature. From the work of Pizzi (Ref 31) the time to bring about "fixation" in chromium/arsenic/D(+) glucose systems as a model reduces rapidly with increasing temperature (Figures 8). Work carried out in Hickson laboratories with wood treated with CCA oxide C shows similar temperature dependence for fixation of Cu and Cr (Figures 9 and 10).

4.2 Concentration

Generally the rate of a chemical reaction with other variables constant, is directly proportional to some power of the concentration of the reactants. A rate equation illustrating this effect is shown first in Figure 7 (Ref 9). However, since there is an excess of reducing chemicals in wood, this equation can be simplified to the second one which shows that in dilute solution the rate of chromium reaction increases as the square of its concentration. However, with solutions concentrations used in treatment at North American treatment plants the simplified rate equation is not relevant until the later stages of fixation when the concentration of chromium VI has fallen significantly. For practical purposes the concentration of the treating solution does not significantly affect fixation time.

This effect is further shown in Figure 11 for arsenic fixation which is dependent on chromium reduction (Ref 40). It also shows that with enough time, the reaction at all concentrations is essentially completed, and for a three-fold reduction in concentration only a modest 16% increase in fixation time occurs.

4.3 pH

Although the effect of pH on CCA reaction is intertwined with the effect of the solution concentration (as the concentration increases the pH decreases), investigations have shown this effect is very small on overall fixation rates unless a large excess of an inorganic acid is added to the CCA.

4.4 Wood species

As part of a comprehensive study on CCA fixation, Wilson of Hickson measured the effect of a few wood species as a variable. Although the effects are usually small, they can be significant for some species. The curves in Figure 12 illustrate this effect.

4.5 Salt versus oxide

The theoretical fixation rates of CCA salt formulations and CCA oxide formulations are about the same, with a slight edge toward the oxide. However, this variable is not very significant.

4.6 Chemical form of X in CCX

Copper chromate based preservatives come in a wide range of different forms (Figure 13).

The rates of fixation of some of these products have been studied in our laboratories and exhibit some interesting differences from CCA. For example with CCB, chromium and copper fixes much more slowly than in CCA (Figures 14 and 15).

4.7 Ratio of copper/chromium/arsenic

In comparing the various ratios of the component oxides for three formulations (Figure 16), we note that the copper ratios are essentially constant. Therefore, one expects Type A to be the fastest reacting formula since it has the highest chromium followed by Type C and then Type B. However, the amount of free CrO_4 in Type A may reduce the apparent fixation rate.

4.8 Added reducing agents

The industrial process of repeated pressure impregnation of lumber with chromated aqueous preservative solution brings about an increase in the levels of extractants in the treating solution. Many of the extractants can be classified as organic reducing agents.

As the concentration of these extractants increases so the rate of fixation (precipitation) of chromated preservatives increases until the phenomenon known in the industry as "sludging" begins to occur in the treating solution. Just as with fixation of CCA in the lumber, the process of sludge formation is temperature, time and concentration dependent.

The work of Rak and Clarke (Ref 35) amply illustrates these effects, in model systems and the work mentioned earlier by Pizzi, Dahlgren and Hartford, et al on mechanisms of reaction of CCA with model systems and wood equally applies in principle to the process of sludge formation.

4.9 Moisture content

In a paper by Pizzi and Conradie (Ref 33) results were presented which indicated reduced permanence of CCA preservatives in wood subjected to high temperatures (80-120°C) immediately after treatment.
An interpretation of this phenomenon is that the mechanism of fixation is affected once the "forgotten" component, water, in the reaction system is removed.

The role of water in fixation of chromated preservatives must not be ignored since the reactions are essentially ionic.

5. THE PRACTICAL IMPLICATIONS OF RAPID FIXATION

5.1 Comments

Factors affecting fixation mentioned in Sections 3 and 4, are the only essential variables which need considering when trying to rationalise fixation of CCA in lumber.

In summary the key factors are moisture content, temperature and time and in simple terms they are the only factors worthy of consideration in production of CCA treated lumber.

How can these factors be brought into play in practical ways such that the wood treater is able to tune his production to accept modified procedures?

Before proposing possible alternatives and to assist the treater in considering how he could best use this technology the next section discusses the variety of means by which the combination of temperature and time may be optimised to bring about fixation.

5.2 Alternative approaches to rapid fixation

5.2.1 Hot air heating

The hot air heating approach is often loosely described as kiln drying. For reasons explained below the term kiln drying is not favoured.

To bring about fixation a heating schedule has to be selected so that the timber will be free of surface defects and resin exudation. Restrictions on the heating schedule are introduced to prevent drying which is too rapid and could impair fixation and efficacy. Work by Pizzi and Conradie (Ref 33) showed the deleterious effect on fixation of rapid laboratory drying of small samples of CCA treated timber.

In addition work by various authors (Refs 2, 4, 18, 41, 43) has shown that if CCA treated timber is dried at high temperatures a reduction in strength can occur. A suggested temperature limit for kiln drying of CCA treated Southern Yellow Pine is 70°C. Work by Winandy (Ref 42) showed that delay between treatment and drying had no significant effect on toughness of treated timber. Lewis (Ref 16) suggests that dehumidifying kilns are the best type for maintenance of strength properties.

In order to confirm the environmental acceptability of kiln drying of CCA treated timber, Williams and Bridges (Ref 39) measured copper, chromium and arsenic levels in the vent during kiln drying; no significant amounts of the elements were present. Water drained from the kiln was found to contain 15-30 mg/l total metallic elements, this water can be used for preparation of treatment solutions.

Edlund (Ref 13) compared the appearance of timber after conventional kiln drying for 16 days at 35-40°C at 60-20% relative humidity and after vacuum kiln drying for 2 days at 79°C, 70-75% relative humidity. Acceptable moisture gradients and no difference in appearance was noted between the two systems.

A kiln schedule has been established to fix and dry CCA treated European Redwood in 8 days total time (Table 1).

5.2.2 MSU fixation PROCESS (Ref 22)

In this process lumber is treated by an empty cell process. After treatment the temperature of the lumber is raised by application of hot water under pressure and fixation is brought about prior to kick back of excess treatment solution.

Work by Wood, Kelso, Barnes, Parikh (Ref 45) compared a conventional full cell treated timber with timber treated and fixed by the empty cell MSU hot water fixation process. CCA oxide C was used with Southern Yellow Pine. No differences in mechanical strength, distribution, proportionation or leach resistance were found.

Barnes (Ref 3) found using Lodgepole Pine preservative gradients were equivalent on treating by full cell or MSU with initial air pressure up to 30 psi. Electron micrographs showed no difference in elemental fixation.

5.2.3 Steam injection

Acceleration of fixation of chromated preservatives by application of steam was first mentioned in 1927 by Gilbert Gunn in a British patent for copper/chrome preservatives (Ref 21). Later steaming was examined by McMahon, Hill and Koch (Ref 17) and patented by Wolman in 1959 (Ref 44).

Studies by Koukal (Ref 16) used steam at 100°C to accelerate fixation.

Subsequent work by various authors (Refs 1, 23-26, 34) used super-heated steam at 110-120°C. One hour steaming was found to be sufficient to induce complete fixation. Peek and Willeitner (Refs 23-26) and Preston and McKaig (Ref 34) found that no reduction in efficacy of CCA treated softwoods occurred on steaming. There was some evidence that steamed hardwoods may be more susceptible to decay than unsteamed. Peek found that the strength properties of treated timber were unchanged by 1 hour's steaming. Barnes (Ref 1) showed that application of super-heated steam for excessive times of 6 hours caused a similar reduction in modulus of rupture for both treated and untreated timber.

Treatment of Spruce at 100°C, or above, is possible without adversely affecting the surface appearance and commercial steaming plants operated in Holland at temperatures of 100°C. However, with Southern Yellow Pine resin exudation occurs above 80°C causing unsightly green flecks where resin reacts with preservative.

Recent work has examined fixation below 100°C. Peek and Willeitner (Refs 27, 38) showed that fixation occurred within 40-50 minutes at 85-90°C. Wagner, Marx and Hettler (Ref 36) used a surface temperature at 85°C for 1 hour to achieve fixation of CBC in a commercial steaming chamber. Cooper and Ung (Ref 5) showed that 12 hours at 50-60°C gave equivalent fixation of CCA in Red Pine poles to that obtained in 20 days at 21°C.

To confirm the environmental acceptability of steaming CBC treated timber, Wagner, Marx and Hettler (Ref 36) tested the steam for copper and chromium and showed that none could be detected. Several workers (Refs 28, 36, 37) have measured levels of copper and chromium in condensate and shown that the condensate can be utilised in the preparation of fresh preservative treatment solution. This information is used to show that timber subjected to accelerated fixation can be used without a waiting period.

5.2.4 Hot oil

In Scandinavia in the early 1970's the 'Royal Process' was invented by B Hagar. This process uses hot oil as the heat transfer medium and in combination with vacuum drying in special oils and pigments is recommended for producing high quality exterior durable cladding/weatherboard. The use of the Royal Process was last reviewed by Edlund in 1985 (Ref 12). Later reports on its use suggest that chromated preservatives are not suitable for use in the process.

6. PRACTICAL APPLICATION OF ACCELERATED FIXATION TECHNOLOGY TO WOOD PROTECTION PLANTS

In the preceding section four methods of bringing about rapid fixation are briefly outlined. In this section the factors of:

- ease of use
- capital cost
- suitability of purpose

are discussed.

6.1 Hot air heating

This process, when based on traditional kilns, uses relatively well established criteria and can readily be fitted into existing wood treatment yard practices. Its main benefits are familiarity, relative ease of operation and likely low maintenance costs.

The disadvantage of hot air fixation are:-

(i) the process takes at least 96 hours at 40°C, with Baltic Redwood

(ii) lumber has to be accumulated before kilns are loaded

(iii) handling processes increase considerably

Capital costs of kilns sized to meet the output from a 30,000,000 BF/year pressure treated wood operation is estimated to be $US500,000.

The operating costs for hot air heating for consumables ie energy, assuming gas fired boilers, is $1.33/1000 BF. (NB This does not include any component of energy cost for drying; this would increase these costs considerably.)

6.2 Hot water fixation

As envisaged by MSU (Ref. 22) this process involves using the CCA treatment cylinder as a fixation chamber. The process in its public form would appear to pose some interesting process, engineering and capacity limitation problems which may require considerable further refinement to bring the process to full practical application in lumber treatment. The main benefits of the process are that it limits the handling of soluble chemicals outside of the treatment area, it fits relatively well with accepted industry practices and it minimises multiple handling of both unfixed and fixed treated product.

6.3 Steam fixation

A considerable amount of technical, production and operating experience is available from steam induced rapid fixation processes operating in Europe. The technology is particularly well developed in Holland, Western Germany and Denmark. The Danish Wood Treating Company, is offering vacuum/steaming which in conjunction are claimed to permit drying. Hickson in Holland have licensees operating steam fixation units which are coupled with zero discharge requirements to meet the extremely stringent environmental standards imposed by the Dutch Authorities. Several treaters, using CBC, have been operating with steam fixation using procedures developed in conjunction with Drs Willeitner and Peek. The West German modern experience is over the last 3 to 5 years and has shown the feasibility of the process. Steaming offers a logical solution in combining the benefits of:

- high thermal capacity
- high latent heat of condensation
- low re-cycled water
- low sludge formation

In common with most treatments involving treating wood it is necessary to carefully control operating temperatures to avoid excessive:

- degrade
- resin mobilisation

Capital costs of steam fixation production units are estimated to be $500,000 for 30,000,000 BF/year operations and operating costs amount to $7.8/1000 BF.

The time to bring about fixation using steam is sensitive to:

- profile of the lumber
- configuration of the pack

If the lumber is stickered then fixation through the whole pack and within each stick of 2" x 4", Southern Yellow Pine can be achieved within one hour at a surface temperature not exceeding 70°C. With Norway Spruce roundwood fixation is achieved in around 1 hour at 90°C.

With block stacked Southern Yellow Pine a steam time of 1 hour is recommended and hold time of 24 hours will be sufficient to result in complete fixation. The pattern of stickering for block stacked lumber is given in Figure 17. The temperature profile in the pack is given in Figures 18 and 19. The effect of steaming on fixation is given in Figure 20. It shows clearly that 1 hour steam and 24 hours standing with the configuration given in Figure 17 is sufficient to fully fix CCA treated lumber.

Steam fixation offers a viable alternative to either standing lumber to fix under ambient conditions or using kilns for hot air heating.

6.4 Hot oil heating

Very little information is available on the commercial use of this process with chromated preservatives. From what is available it is evident that:-

(i) the process is not considered suitable for chromated preservatives

(ii) it is only being used with ammoniacal copper caprylate and in plants handling only around 2,000,000 BF/year.

6.5 Summary of capital, operating costs

See Figures 21 and 22.

7. CONCLUSIONS

The foregoing presentation of information has demonstrated that practical experience is available to enable rapid fixation to be used in production scale operations. The number of operating fixation plant in Northern Europe is estimated to be between 10 and 20. The interest in and rate of acceptance of this technology has increased dramatically in the past two years. With increasing environmental responsibility being the catch phrase, industry, developments in this area are vitally important in providing alternative means of meeting increasingly tight environmental control standards.

The wood treater is faced with deciding how best he can reduce the environmental impact of wood treating to the increasingly severe requirements imposed by the regulators. There is no "best solution" but there are a number of technologies available from which the treater can select that option which will best suit his needs, eg if he has redundant kiln capacity then hot air heating may well supply the most cost-effective approach; if he is space limited then steaming or the MSU process could well be most suitable.

Ultimately, as it should be, the treater will have a range of choices open to him. It is up to the chemical and equipment suppliers to ensure that he is provided with all the information necessary for him to arrive at the optimal solution for his needs and not to try to sell him unsuitable technology.

Hopefully this paper will help the treater to be more aware of the options he has and to be able to seek out the answers to his problems from the most informed sources.

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FIXATION AND DRYING CYCLES
CCA TREATED LUMBER

SPECIES	TEMPERATURE & R.H.			TIME	EFFECT
	Dry Bulb °C	Wet Bulb °C	R.H. %	days	
BALTIC REDWOOD	40	35	70	4	Fixation
	40	32	55	4	Drying

TABLE 1

pH v Time v Temperature

System :Cu/Cr/As/D(+)-Glucose

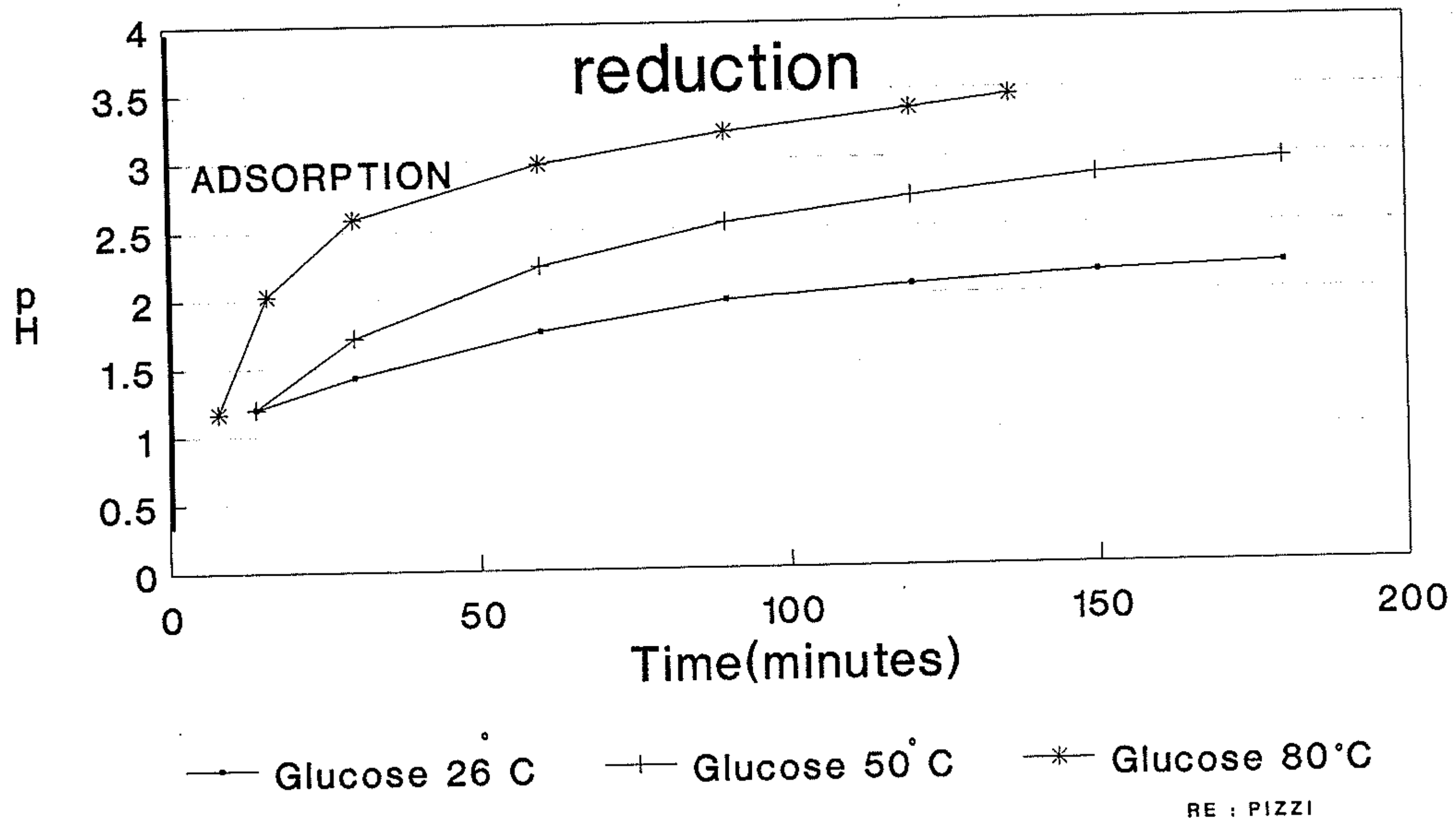
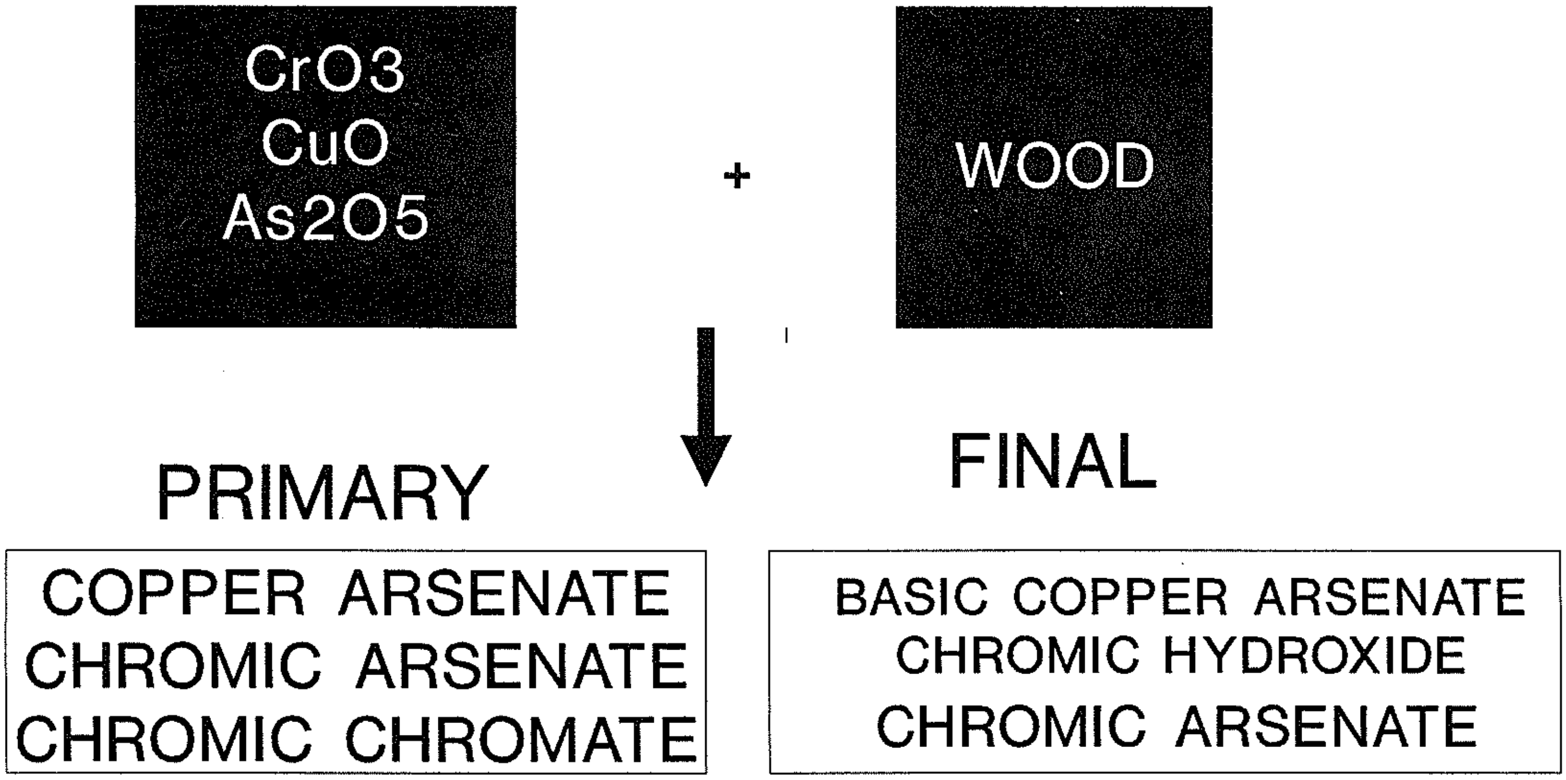


Figure 1

CHROMATED COPPER ARSENATE TYPE C
FIXATION PRODUCTS



CrO3
CuO
As2O5

+

WOOD

PRIMARY

COPPER ARSENATE
CHROMIC ARSENATE
CHROMIC CHROMATE

FINAL

BASIC COPPER ARSENATE
CHROMIC HYDROXIDE
CHROMIC ARSENATE

Figure 2

Re : Dahlgren & Hartford

COPPER ARSENATES

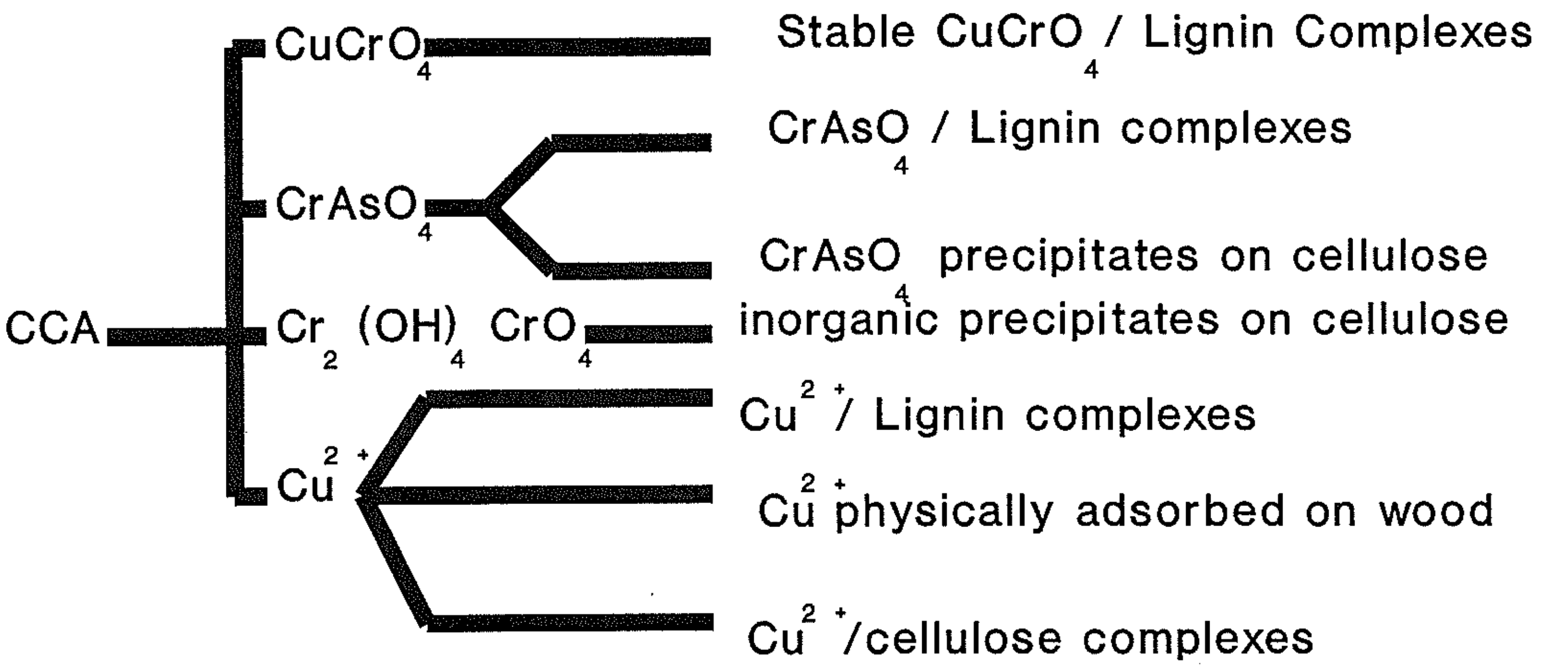
Effect of pH on Compounds

pH	Chemical Formula	Name
< 1	$Cu(H_2AsO_4)_2.2H_3AsO_4$	Acid Copper Arsenate (double salt)
< 2.8	$CuHAsO_4.H_2O$	Acid Copper Arsenate
2.8 - 3.2	$Cu_3(AsO_4)_2.4H_2O$	Copper Arsenate
> 3.2	$Cu(OH).CuAsO_4$	Basic Copper Arsenate

RE : DAHLGREN & HARTFORD

Figure 3

CCA REACTION PRODUCTS



CCA

$CuCrO_4$

$CrAsO_4$

$Cr_2(OH)_4CrO_4$

Cu^{2+}

Stable $CuCrO_4$ / Lignin Complexes

$CrAsO_4$ / Lignin complexes

$CrAsO_4$ precipitates on cellulose

inorganic precipitates on cellulose

Cu^{2+} / Lignin complexes

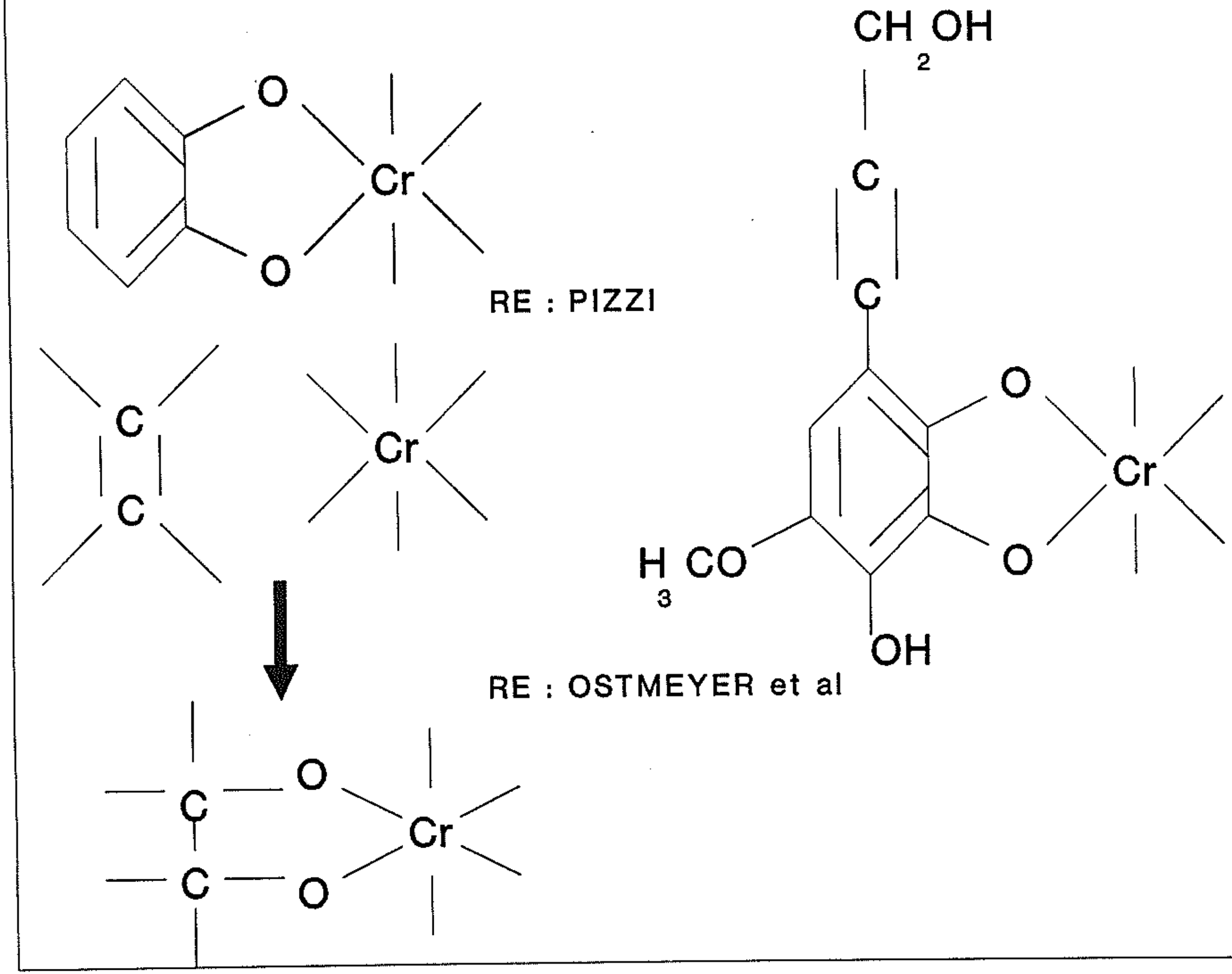
Cu^{2+} physically adsorbed on wood

Cu^{2+}/cellulose complexes

Figure 4

RE : PIZZI

POSSIBLE WOOD CHROMATE ESTERS



RE : PIZZI

RE : OSTMEYER et al

Figure 5

FACTORS AFFECTING FIXATION

- TEMPERATURE
- CONCENTRATION
- pH
- WOOD SPECIES
- SALT vs OXIDE
- CHEMICAL FORM OF X IN CCX
- Cu/Cr/As RATIO
- ADDED REDUCING AGENT
- MOISTURE CONTENT

Figure 6

EQUATIONS RELEVANT TO CCA FIXATION

RATE EQUATIONS

(i) $$\frac{-d[Cr(VI)total]}{dT} = k_1[HCrO_4^{\ -}] \cdot [H^+]^2 \cdot [x]$$

k_1 = Rate constant
x = Compound being oxidised
T = Time

(ii) $$\frac{-d[Cr(VI)total]}{dT} = k_2[Cr(VI)]^2$$

k_2 = Rate constant

(iii) ARRHENIUS EQUATION

$$k = Ae^{\frac{-E}{RT}}$$

A = CONSTANT
E = ACTIVATION ENERGY
R = GAS CONSTANT
T = TEMPERATURE K

Figure 7

Fixation Time v Temperature

System : Cr/As/D(+)-Glucose

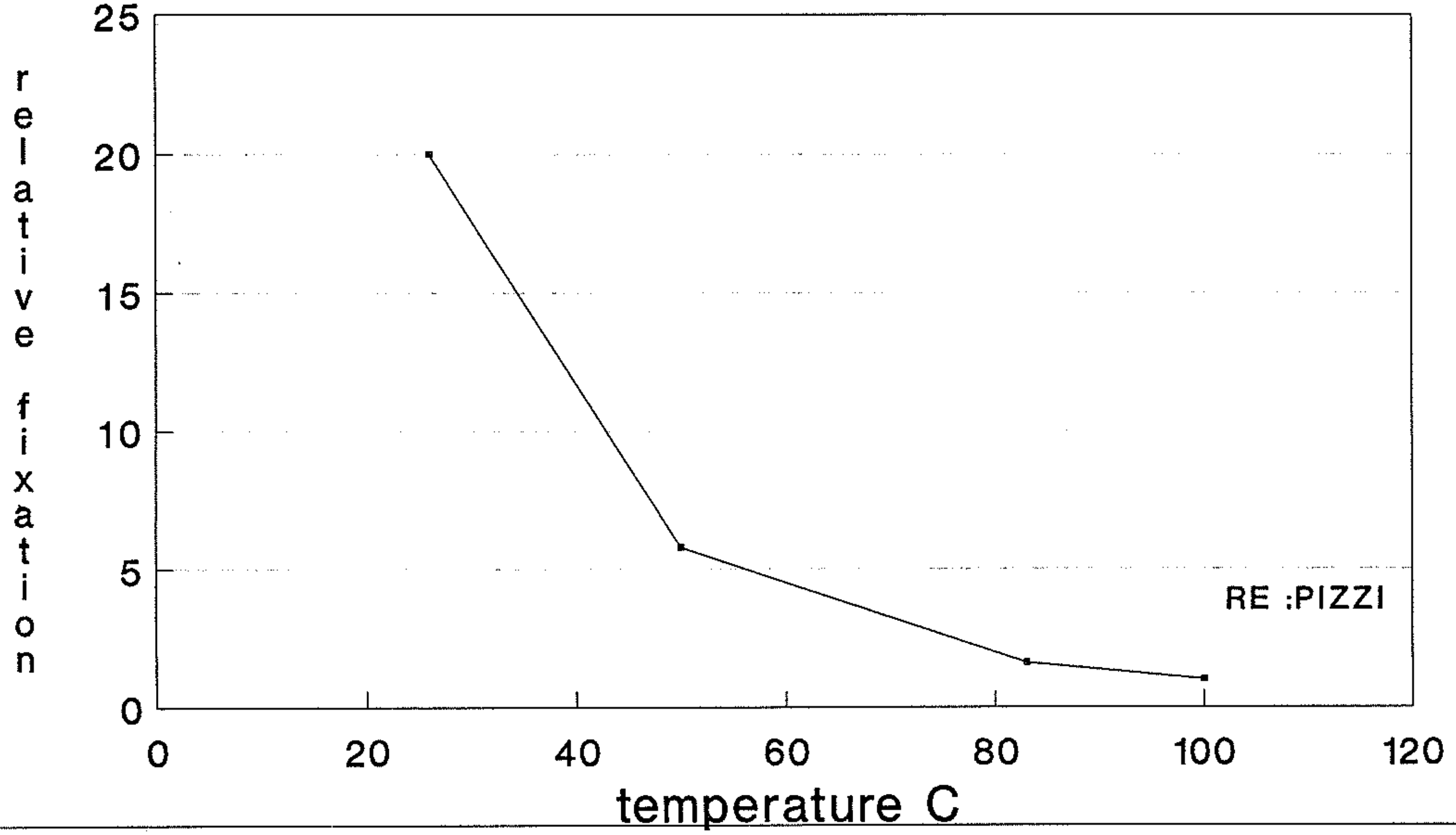


Figure 8

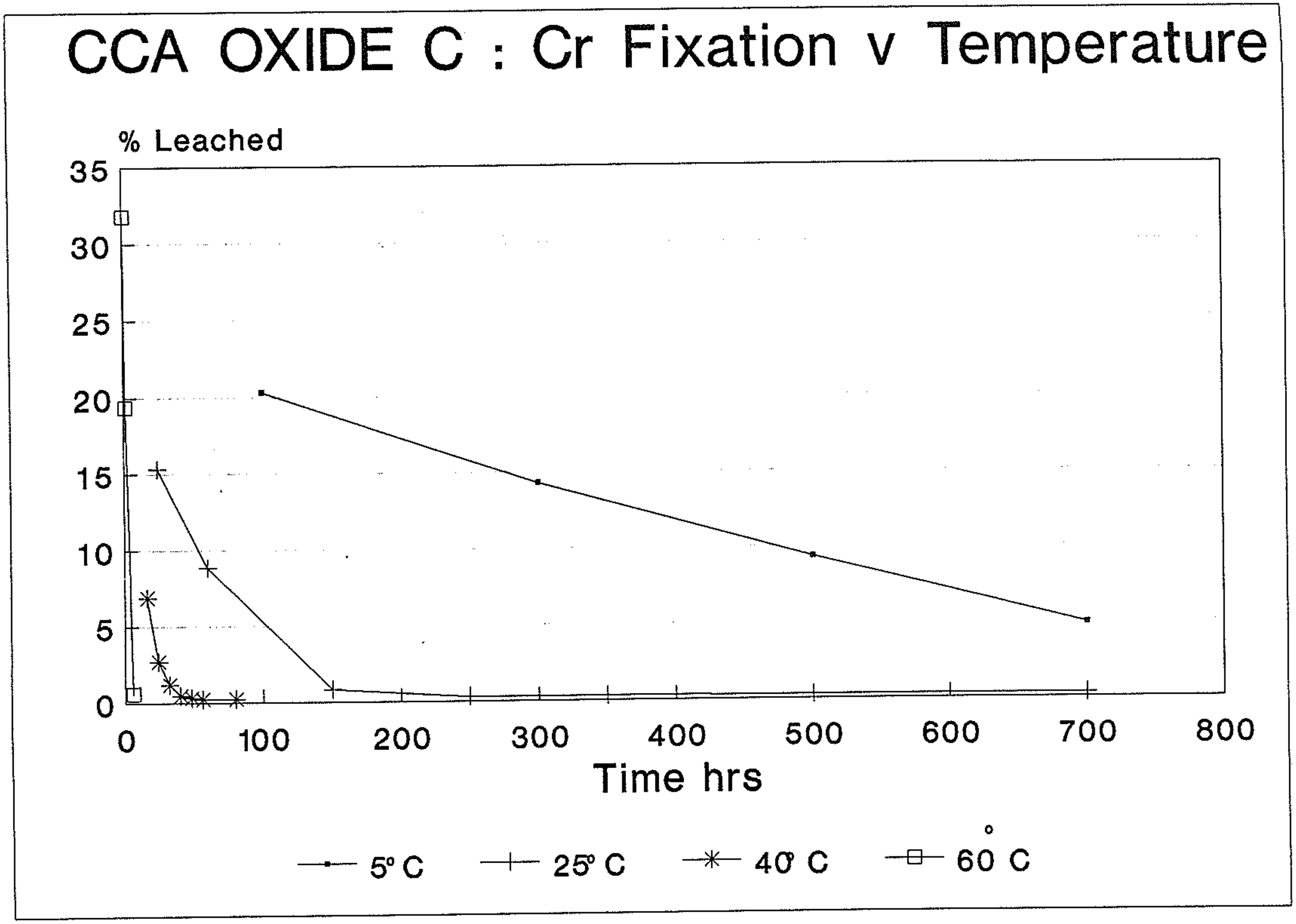
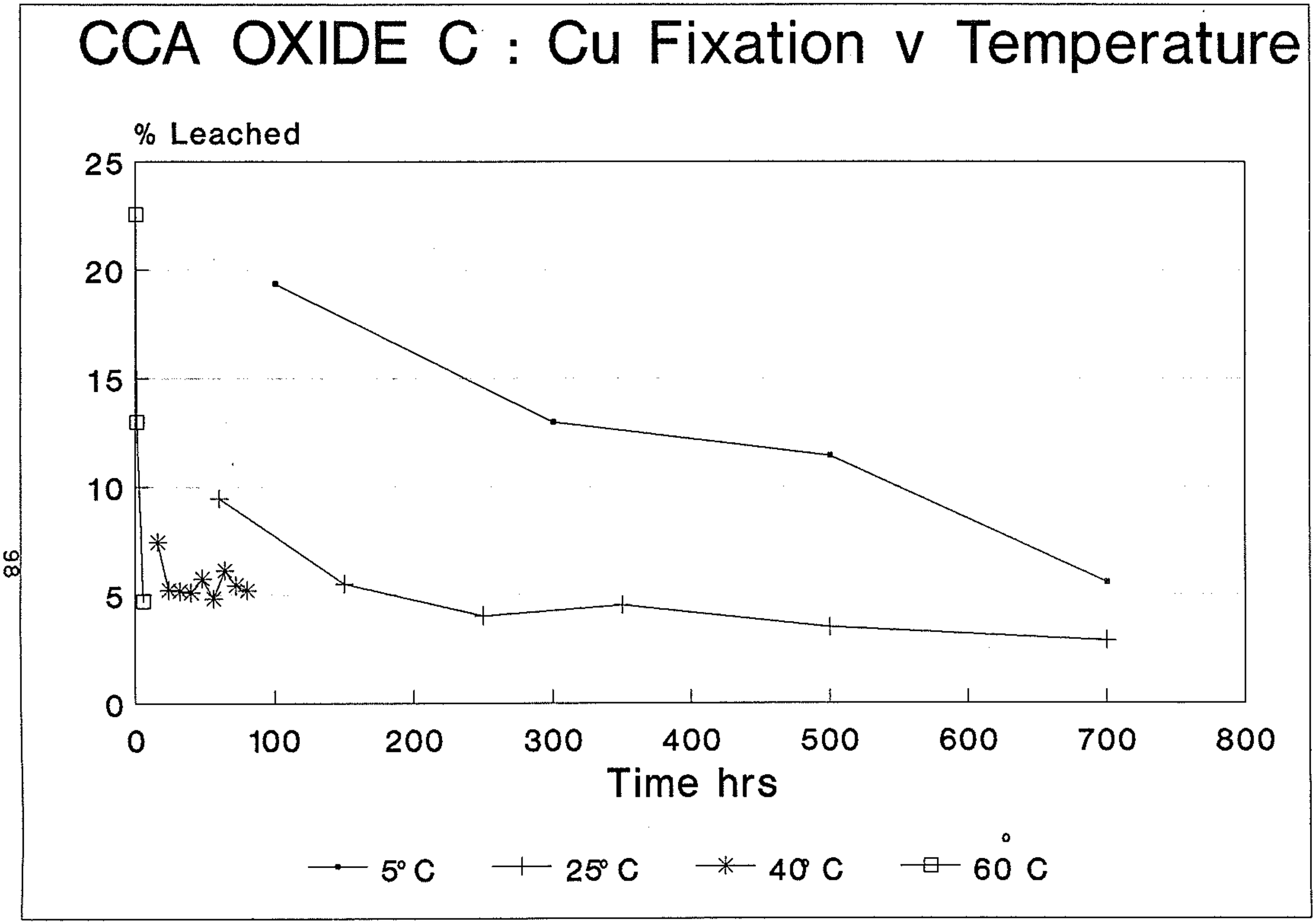

CCA OXIDE C : Cr Fixation v Temperature
% Leached
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
Time hrs
5° C
25° C
40° C
60° C

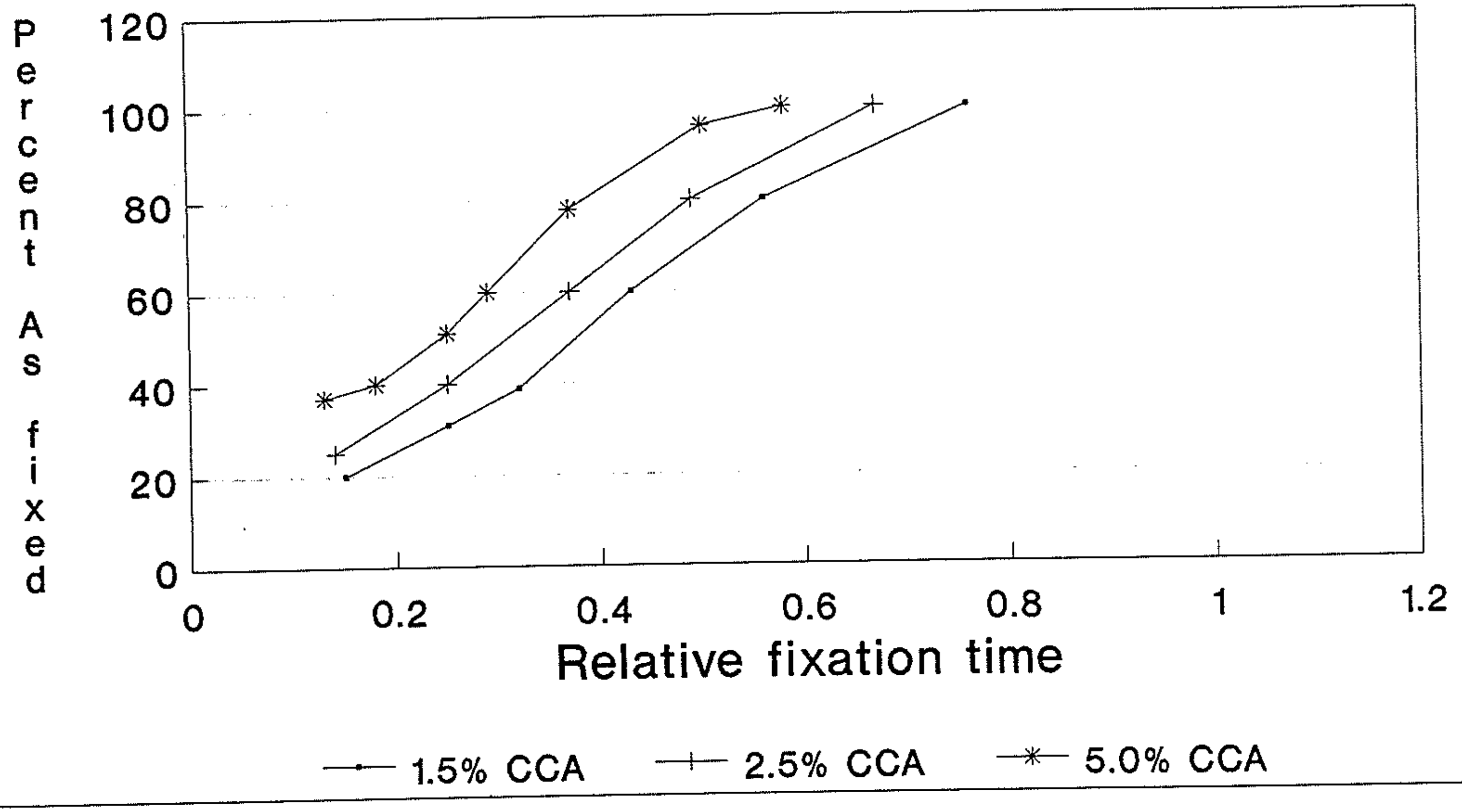
Figure 9



CCA OXIDE C : Cu Fixation v Temperature

Figure 10

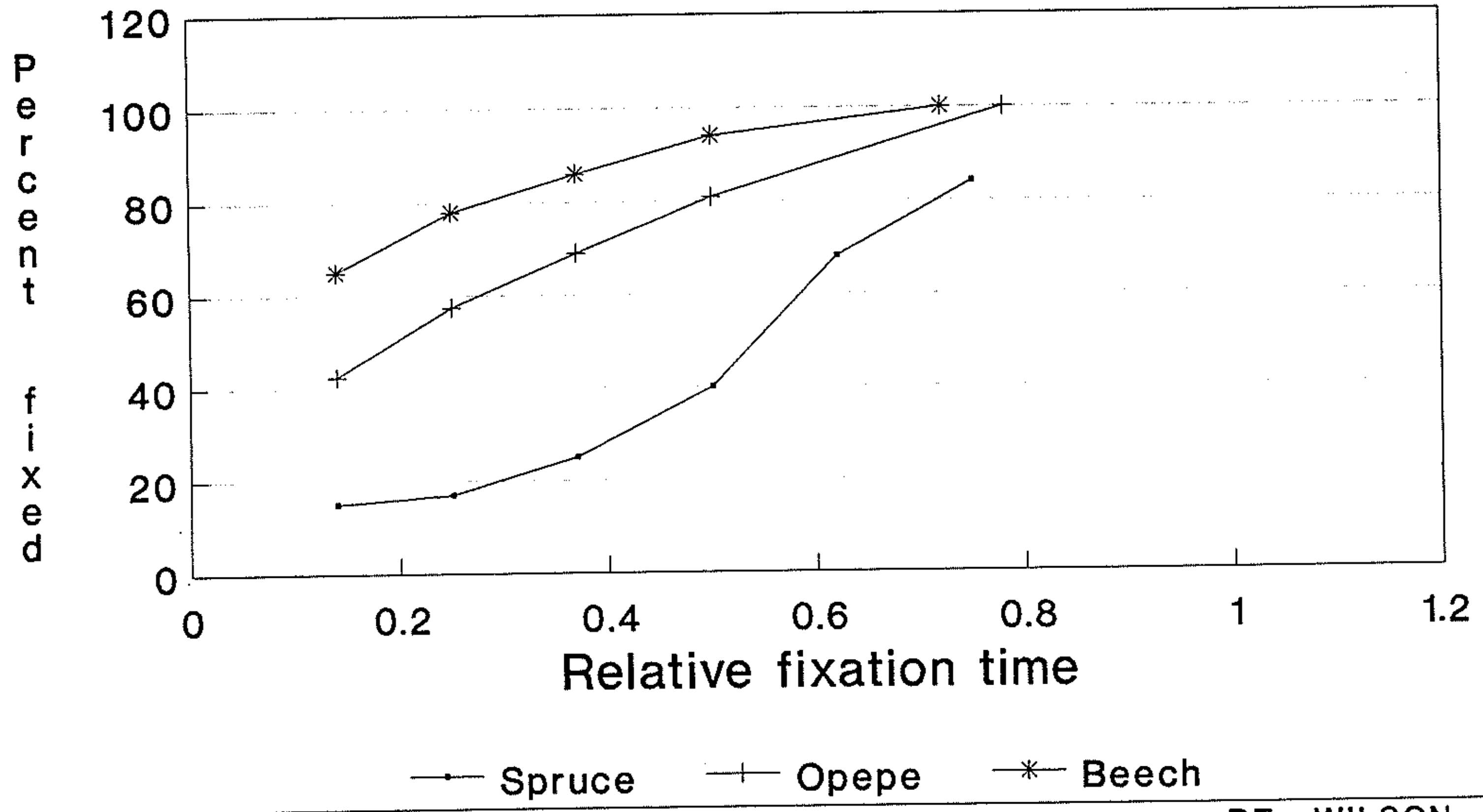
Concentration
Effect on Fixation



RE : WILSON

Figure 11

Species
Effect on Fixation



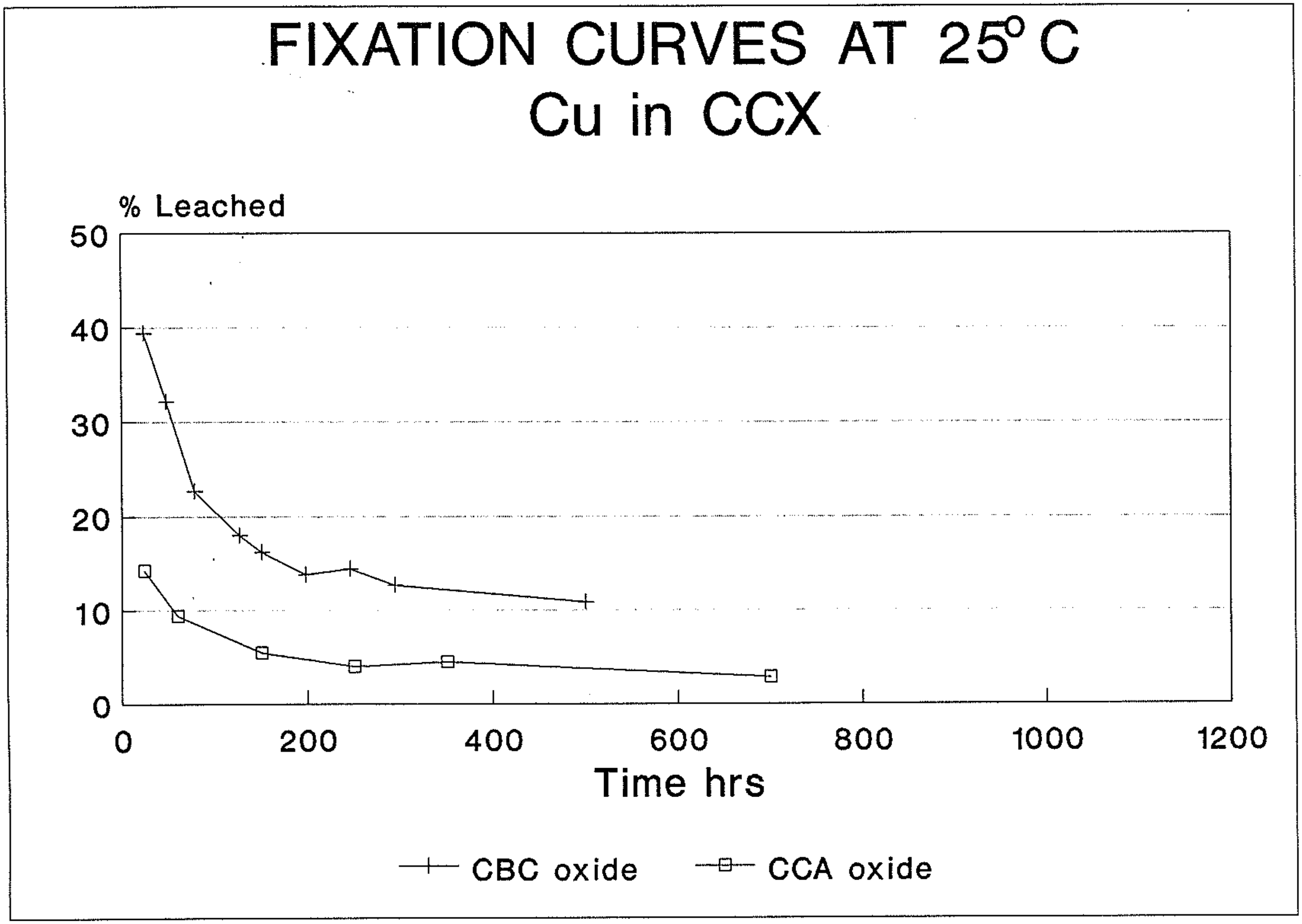
RE ; WILSON

Figure 12

CHEMICAL FORM OF X IN CCX

Chemical name	Abbreviation	X
Copper Chromate	CC	None
Chromated copper arsenate	CCA -A CCA -B CCA -C	Arsenate
Chromated copper borate	CCB	Borate
Chromated copper phosphate	CCP	Phosphate
Chromated copper hexafluorosilicate	CFK	Hexafluorosilicate

Figure 13



FIXATION CURVES AT 25° C
Cu in CCX

Figure 14

FIXATION CURVES AT 25° C
Cr in CCX

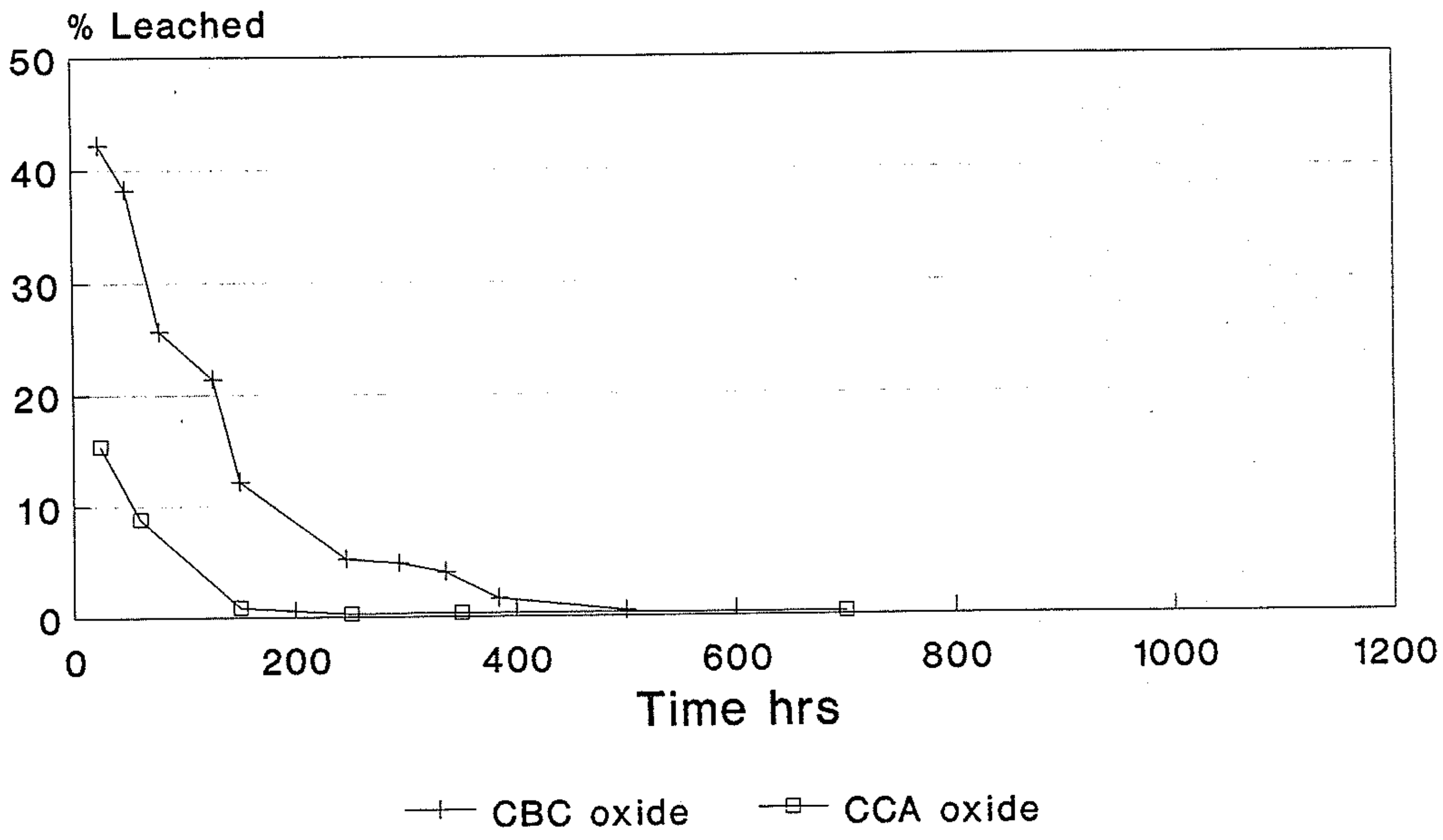


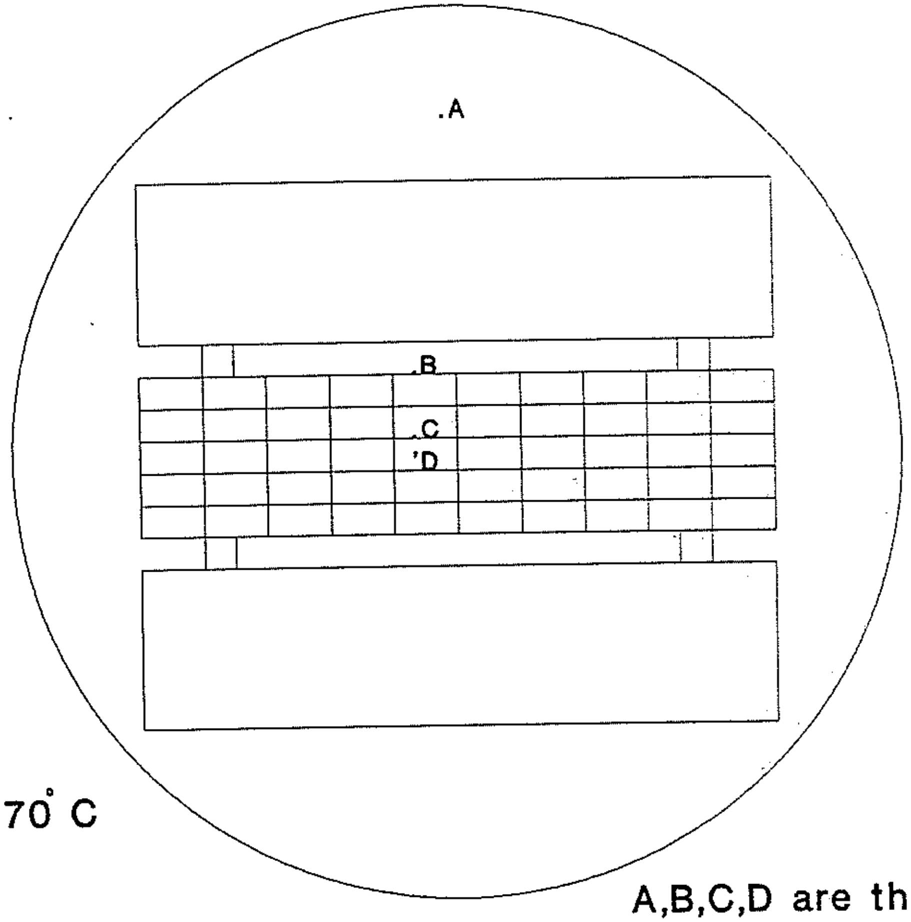
Figure 15

CCA OXIDE FORMULATIONS
% OXIDE

OXIDE	TYPE A	TYPE B	TYPE C
CrO_3	65.5	35.3	47.5
CuO	18.1	19.6	18.5
As_2O_5	16.4	45.1	34.0

Figure 16

ARRANGEMENT OF BOARDS FOR STEAMING



cycle : 1-2 hr @ 70° C
@ B

A,B,C,D are thermocouple sites

Figure 17

TEMPERATURE v TIME IN STEAMING CYCLE

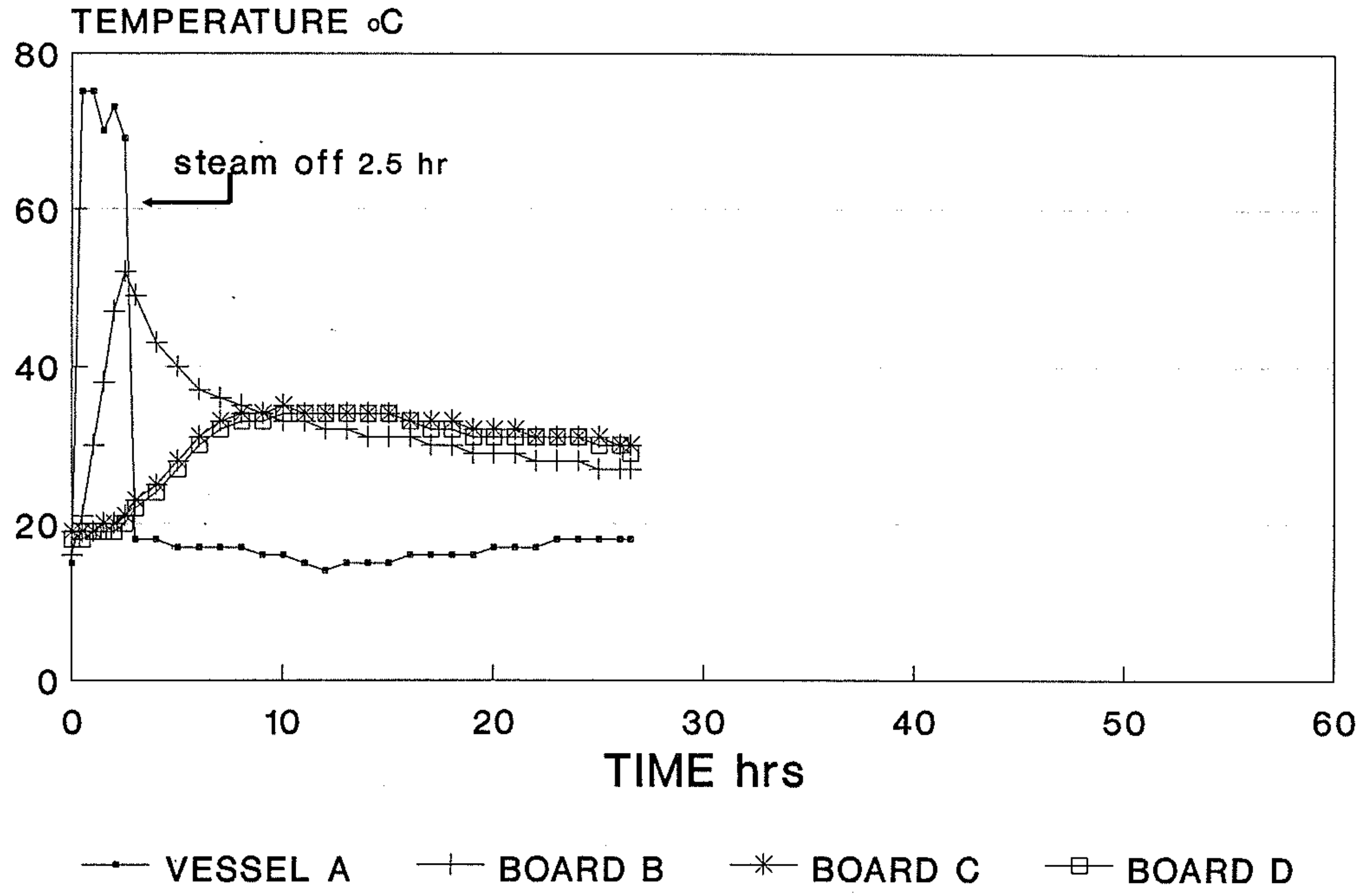


Figure 18

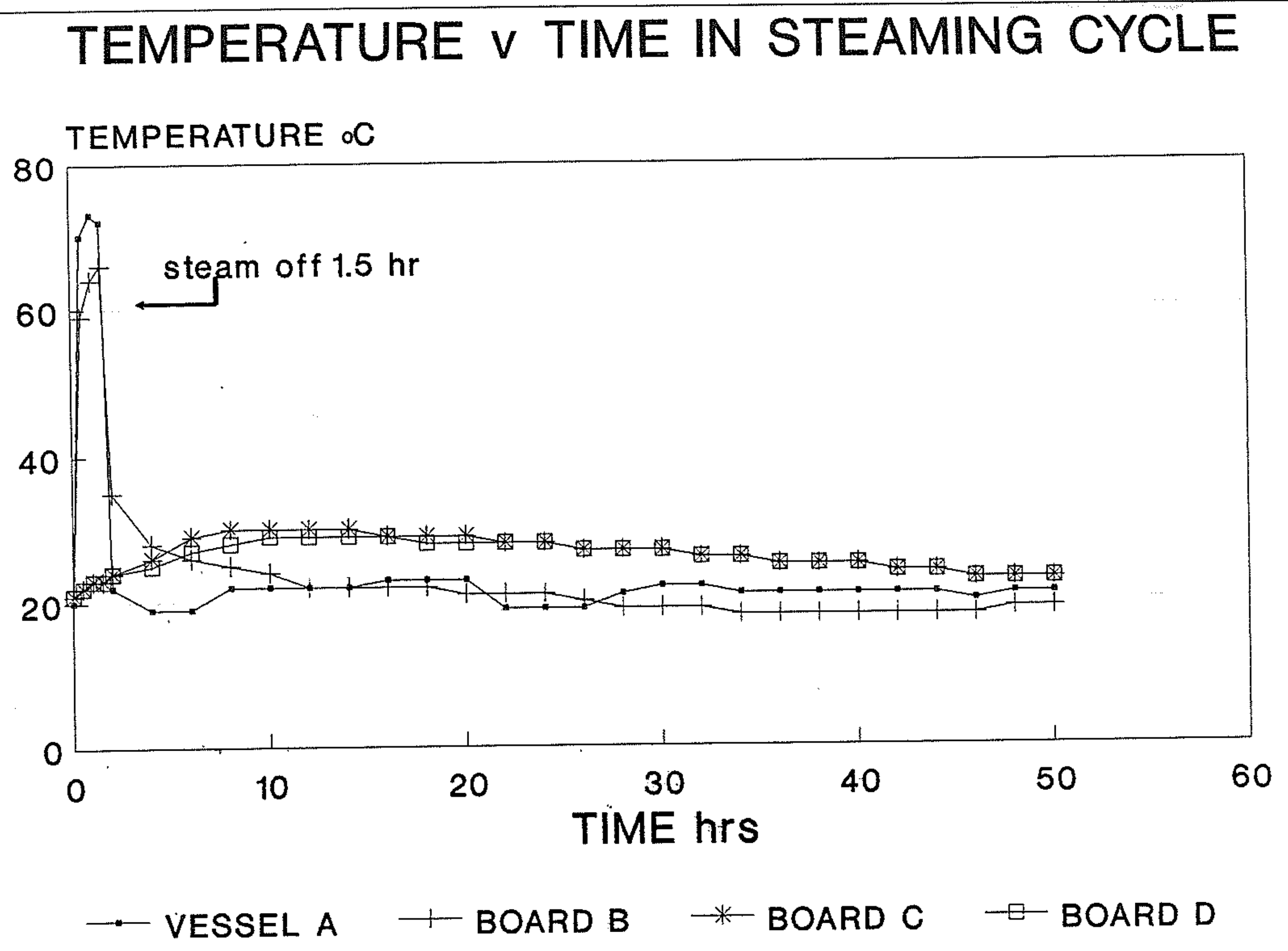

TEMPERATURE v TIME IN STEAMING CYCLE
TEMPERATURE oC
80
60
40
20
0
steam off 1.5 hr
0
10
20
30
40
50
60
TIME hrs
VESSEL A
BOARD B
BOARD C
BOARD D

Figure 19

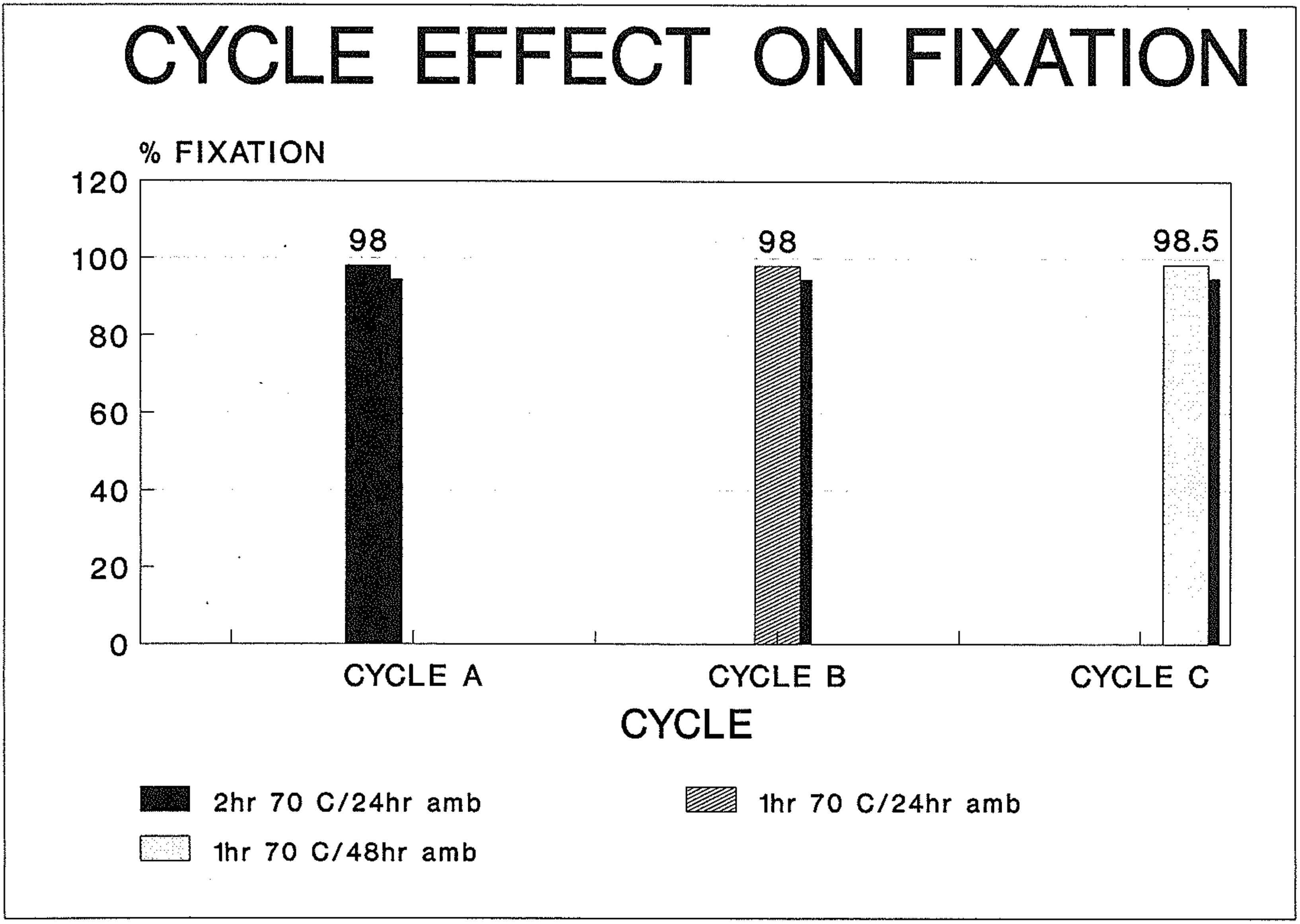

CYCLE EFFECT ON FIXATION
% FIXATION
120
100
80
60
40
20
0
98
98
98.5
CYCLE A
CYCLE B
CYCLE C
CYCLE
2hr 70 C/24hr amb
1hr 70 C/24hr amb
1hr 70 C/48hr amb

Figure 20

ESTIMATED OPERATING COSTS FOR THREE FIXATION SYSTEMS.

30,000MBF/yr	HOT AIR cost/yr	MSU cost/yr	STEAM cost/yr
ENERGY	$40000[2]	$34000[3]	$25000[1]
LABOUR	$111000[5]	$83000[4]	$83000[4]
CAP.CHGS			
DEP.	$50000[6]	$120000[7]	$50000[8]
R.o.A.	$75000	$180000	$75000
TOTAL COST	$276000	$417000	$233000
$/MBF	9.2	13.9	7.8

Figure 21

OPERATING COST ASSUMPTIONS

Footnotes to Figure 21

(1) Steaming energy usage based upon data from European plants, where steam usage is 162lbs/MBF.

(2) Assumes no drying and 60% more energy usage than (1)

(3) Assumes 33% greater energy usage than steam due to fixation cycle being three times longer.

(4) Based on 3 men , @ 2400 std hrs/yr + 15% premium hrs per man.Hourly rates , $10 std., $12.5 premium.

(5) One extra man allowed for kiln loading.

(6) Capital $500,000.

(7) Capital $1,200,000.

(8) Capital $500,000.

Figure 22