A MANUFACTURER'S OPINION ON THE CAUSE OR EFFECT ON COLOURING CONCRETE

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Introduction

The production of coloured concrete has proven to be an art and this is essential if Concrete Block Paving is to penetrate further into the market.

Coloured concrete requires an evenly coloured surface that will last. Colour has for thousands of years been used for visual effect. People have painted their skins, even men and women today change their pale skins to brown or suntan by coloured powder. The Romans used various colours in their mosaic patterns to illustrate and make pictures. Nothing has really changed over the last two thousand years, today we colour our concrete products to satisfy the whims of the specifiers from very dark colours through black to red to yellow.

The purpose of colouring concrete is to create something a little more permanent than a simple surface coating, but is it possible to fully meet the expectations of obtaining a permanent colour?

Background

We all have an idea that many aspects of concrete mix design, surface texture and pigmentation levels have an effect on the colour of concrete but we never have evaluated them. The following information, is based on a laboratory evaluation, to demonstrate mainly to the production staff of any company the variabilities that can and do occur in the day to day production.

Brief Explanation of Colour Measurement

With the increasing diversity of colour products, recognition is becoming more and more important. Colour is one of the major factors in creating a product image and has a great effect on sales. Because of this, we must be concerned about colour, and colour control is becoming a part of our strategy. However, in our case, colour is performed by visual evaluation, relying on the accuracy of an individual's eyes to determine colour. Unfortunately, every individual's colour perception is slightly different. Also, it is extremely difficult to accurately describe a colour in words since each person will interpret the described colour a little differently.
Colour is a matter of perception and words have always changed with the times. If we consider Red, we have used common colour names like "vermilion" crimson, scarlet etc but now, we use precise expressions like "bright", "dull" and "deep".

Colour is broken down into three primary elements of their "hue (colour)", "lightness (brightness) " and "saturation (vividness)". This method of expressing colour in three dimension has been used in developing the charts and the notation is used as follows:

L* A* B*

To compare colours, we use colour differentials and Delta E is used to indicate deviations.

Negative numbers means it is duller or darker.
Positive numbers means it is brighter or lighter.

Evaluation

This was a laboratory biased evaluation investigating the comparison of different colours of cements, saturation curves of two pigments, the effect of water content and the effect of slag and pulverised fuel ash additions.

In all the tests, we controlled as many variations as possible to minimise the variations.

The mix used was:

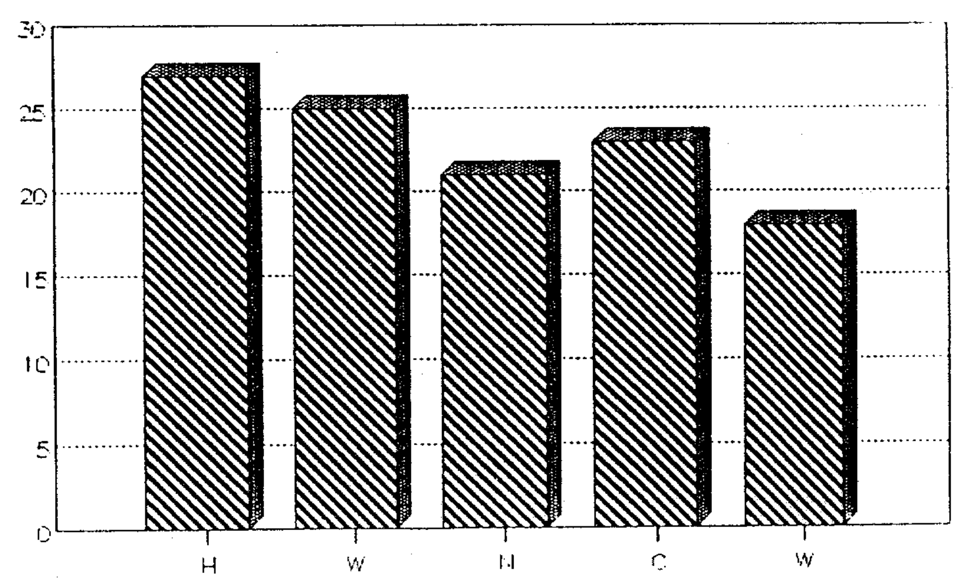
305g Sand
195g 6mm Gravel
100g Cement
40g Water

The curing was in a temperature controlled room and all the samples were made on a laboratory produced press. The colour measurements were made using a Minolta Spectrometer, this measures the lightness factor L* and the chromaticity A* and B*.

Effect of Different Types of Cement

To compare and evaluate the effect of different cements, using the table below, knowing from standard production Hope Cement gave us good colours this was used as the control.

Samples of all cements available to use from Blue Circle Cement was obtained and using the Colour Index Chart a range of cements were chosen to represent the spectrum of colour, the lower the colour the greyer the colour, higher the number the browner the colour.



Effect of Different Types of P F A

The qualities of P F A, vary from power station to power station, dependant on the source of the coal, and the efficiency of the burning.
Variations are shown up in three main areas:

(a) the colour, this affects the colour of the concrete in which it is used,
(b) the presence of free carbonaceous materials, and alkalis, which affect the concrete setting and curing rates, usually adversely, and,
(c) particle size, where an increase causes a reduction in the setting rate.

Powdered Pigments

The pigments commonly used in concrete are mainly the various oxides of iron, plus a little cobalt blue and chrome oxide green. The latter are expensive and so are not used very often.
Some carbon black, phthalocynaine blue and phthalocynaine green are used. These however have suspect durability. They tend to lose colour by leaching from the concrete, and also by oxidation.
Some naturally occurring oxides as ochres etc., are used, but the bulk of pigments used in the concrete industry today, are synthetic.

(a) Yellow Iron Oxide (FeO.OH)

This is mainly produced by modified Penniman Zoph processes, which produce pigments having acicular shaped crystals.
Some is produced by an aniline process, which gives a rhombohedral crystal. This type of pigment has two advantages:

(i) Reduced water/oil absorption
(ii) Reduced tendency to orientate in an applied paint (silking)

The colour is controlled by the crystal size, which is usually quoted as an aspect ratio, width x length:

Lemon Yellow - 0.1 x 0.6 microns
Golden Yellow - 0.2 x 0.8 microns

The colour moves towards the red end of the spectrum as the crystal size is increased. Yellow oxides are light fast, but the colour is reddened by heat.
The pigment starts to lose its water of crystallisation at about 150°C and converts to Fe_2O_3, red oxide.

(b) Black Iron Oxide (Fe_2O_3)

Black iron oxide is produced using three main methods:

(i) As a by-product during the production of aniline,
(ii) direct precipitation from copperas ($FeSO_4 7H_2O$) with alkali and heat and,
(iii) the reaction of yellow iron oxide with copperas under hot alkaline conditions

All methods produce spherical particles, with particles size varying between 0.1 and 0.6 microns.

The tinting strength tends to decrease with increase in particle size, and the tone becomes blurred.
Black Iron Oxide is lightfast but under certain oxidising conditions can be converted to red by heating to above 80°C

(c) Red Iron Oxide (Fe_2O_3)

There are four main methods of producing red iron oxides.

(i) Calcination of copperas ($FeSo_4 7H_2O$) in an oxidising atmosphere.The pigment is lightfast and heat resisting. This method produced round particles that have lower water/oil absorption.

(ii) Calcination of black oxide of iron in an oxidising atmosphere. The pigment has similar properties to the copperas red.

(iii) Calcination of yellow oxide of iron.In this case the acicular particles of yellow are dehydrated, leaving a substantially acicular particle. These pigments are also lightfast and heat resisting, but due to the particle shape, have a higher water/oil absorption.

(iv) Direct precipitation using a modified Penniman-Zoph process.These pigments contain up to about 2% water of crystallisation, which may be lost on heating with a move in shade to the blue end of the spectrum.The particle shape is mainly round, and the pigments have lower water/oil absorptions.

There are wide variations in particle size between 01. to 2.0 microns, dependant on the colour and manufacturing process.
In general the yellower reds have the finer particle size, while the bluer reds are coarser. The precipitated reds have the finer particle size while the calcined reds are coarser. The coarsest reds are the bluer copperas reds. All of these red pigments, however, perform well in concrete applications.

(d) Browns
Browns are normally blends of red and black, or red, yellow and black oxides of iron.

(e) Marigolds
These are blends of yellow and red oxide of iron.

(f) Greens

(i) Blends of yellow and black oxides of iron.

(ii) Blends of yellow oxide of iron and phthalocynaine blue or green.

Wetting Agent Concentration

The vast majority of the powdered pigment supplied to the concrete industry contain no wetting agent.

If a wetting agent or a surface coating were applied to any pigment, it would tend to make it specific for some end use, and limiting to the pigment supplier. Surface coatings and treatments are more commonly found on pigments intended for the paint and plastic markets.

Particle Size and Particle Size Distribution

Many of the methods of measuring the particle size distribution require that a dilute dispersion is produced. During the production of this dispersion, a dispersant and a lot of energy is used, sufficient such that agglomerates and aggregates are broken down to approaching the crystal size. The results are therefore of dubious benefits.

Pigments manufacturers normally quote sieve residuces, either 45 or 63 micron, to indicate the level of oversized particles present in the pigment, and not the actual particle sizes.

Liquid/Slurries

The addition of dry pigment to a concrete mix, has been criticised as:

(i) not environmentally friendly (messy)
(ii) inefficient, the full colour value not being achieved, and,
(iii) lacking in reproducibility.

Complaint number (i) depends to some extent on the concrete making equipment, but is, in the main, valid.
Complaints numbers (ii) and (iii) are also dependant on the equipment, mixing time, and the concrete formulation, and particularly with dry mixes, and short mixing times, are valid.

There are a variety of ways of making a slurry of pigment which will minimise these problems. There is no dry pigment to cause dust. The pigment is pre-wetted when added, so no time is needed for the wetting out.

Metering of a liquid, either by weight or by volume, is relatively easy, accurate and repeatable.

(a) A simple slurry may be produced purely by adding the pigment to water and vigorously stirring. The solid content may have to be kept fairly low if a high water demand pigment is used. The pigment may well still be in a flocculated form, even though the slurry is a liquid.

(b) A better method is to disperse the pigment in water with the help of a dispersing agent. This usually leads to the potential to produce a higher solids, more stable, and less flocculated slurry.

(c) The best method is to produce a dispersion using wetting agents and stabilising agent, and to pass this dispersion through a grinding mill. This will produce an almost 100% deflocculated dispersion, which has the highest staining strength in concrete.

Effect of the Different Cement

Using the standard mix, small units were produced with any pigment and these are referred to in the table as "blanks".
Table 1 gives the individual readings using the Minolta Spectrometer and Table 2 gives the difference in the results and using the formulae

$$AE = \sqrt{L^2 + a^2 + b^2}$$

AE is calculated

The Effect of Pigment Addition on the Colour Factor

We have, on numerous occasions, been told and shown the effects on the colour with increasing amounts of pigment and to demonstrate this using Harcros Pigments YB 3100 and RB 2500, rates of additions varied between 2 and 7% in 1% increments based on cement weights.

Hope Cement was chosen as the cement for cross referencing and table 3 and table 4 gives the readings and difference for both pigments.

The Effect of Water Content on Colour

To observe the effects of water content, Hope Cement and YB 3100 was taken as the control. The water addition was adjusted to give 10% more and 10% less water from the controlled mix.
Table 5 gives the readings obtained and the differences between the results.

The Effects of the Addition of Slag and P F A on the Colour

For this evaluation, Westbury Cement and YB 3100 was used, with the addition rate of p f a and slag constant. In the British Standards, we are controlled as to the amount of cementitious material we can use and in this experiment the cement content was reduced by 20% and a direct replacement using p f a and slag of this 20%.
It was observed that when changing sources of p f a there were colour differences and to demonstrate this two ashes were chosen based on the loss of ignition test. The two levels chosen were 3% and 5% L.1.0.
Two flags from different sources were chosen for these tests.Table 6 gives the readings and the differences.

The Effect of Surface Texture

The original mix was taken but the 6mm gravel level was greatly reduced to observe if there was a colour difference.

Other Factors in Colour Variations

Again, from normal production, we have observed colour difference, so our evaluation of the differences in the chambers were measured in three different works locations.
In this evaluation, three different curing methods were measured using "Tiny Tot" recorders. These are programmable records and can take readings from 10 second to 3 hour intervals.
The curing regimes ranged from one large chamber insulted on the outside sides, back and top with no doors on the front to large chambers split into departments with insulation including doors and to small individual chambers with the ability to recirculate and heat the air.

The following is a precis of the recorded range of values of temperature.

WORKS	LOCATION		
	BOTTOM	MIDDLE	TOP
A	7 - 10		6 - 13
B	14 - 19	19 - 23	17 - 2
C	11 - 30	17 - 30	18 - 30

Further work is being carried out and the results of colour changes will be reported at the workshop.
The graphs illustrate how the temperature changes in the chambers.

Summary of the Evaluation

There was never any intention of making conclusions, only to demonstrate in a particular way that the ultimate colour can be affected by major changes. For example, different cement sources, variability in p f a, water content and curing regimes.

The colour variation is within the control of the manufacturers and that we should at all times exercise control in every way possible.

The following graph illustrates the control levels at the works on the standard devation, mainly due to the curing regime but other factors can and will influence the results.

There are several questions to be asked of ourselves and our material suppliers and they are:-

1. How consistent is the cement and can it be produced with more control?
2. Can we have better or customerised pigments ?
3. Can we have better water control?
4. Can we have better weighing equipment?

Conclusion

Customerised Pigment

A "customer pigment" is a pigment that is not a standard product, but one that has been modified in some way to meet a customer request.

- (a) Tighter Colour Control.
- (b) Special Shade.
- (c) Special Properties
  - (i) a surface coating,
  - (ii) containing a dispersing agent,
  - (iii) specific slurry viscosity,
  - (iv) controlled pH
- (d) Chemical Purity.
- (e) Special Packaging.
- (f) Special Weights etc.

Acknowledgement

1. Harcros Pigments for supplying the pigments, producing the blocks and carrying out the measurements.

2. Blue Circle Cement for supplying the cement and the colour measurement of the cement.

3. Staff at Marshalls, especially Ian Ferguson, Carey Dowson, Colin Nessfield for their contribution in production and David Jessop for producing the graphs.

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Marshalls Concrete Blocks : Dry	Delta E	L*	A*	B*
		Minolta 310		
Blank				
Hope	-	50.47	1.68	7.30
Westbury	-	50.72	1.39	6.40
Northfleet	-	50.20	0.83	5.54
Cauldon	-	48.34	1.21	5.68
Weardale	-	47.92	1.04	5.76
YB3100 - 3%				
Hope	-	51.79	2.22	20.93
Westbury	-	51.72	1.82	20.78
Northfleet	-	51.58	1.34	20.00
Cauldon	-	49.65	1.44	18.48
Weardale	-	49.80	1.21	19.46
RB25000 -3%				
Hope	-	42.12	17.31	15.73
Westbury	-	42.52	17.26	15.41
Northfleet	-	41.54	17.17	15.21
Cauldon	-	41.74	15.82	14.31
Weardale	-	40.21	15.93	15.38

TABLE 2

Marshalls Concrete Blocks : Dry	Delta E	L*	A*	B*
		Minolta 310		
Blank				
Hope	-	50.47	1.68	7.30
Westbury	0.97	0.25	-0.29	-0.90
Northfleet	1.97	-0.27	-0.85	-1.76
Cauldon	2.71	-2.13	-0.47	-1.62
Weardale	3.04	-2.55	-0.64	-1.54
YB3100 -3%				
Hope	-	51.79	2.22	20.93
Westbury	0.43	-0.07	-0.40	-0.15
Northfleet	1.29	-0.21	-0.88	-0.93
Cauldon	3.34	-2.14	-0.78	-2.45
Weardale	2.67	-1.99	-1.01	-1.47
RB2500 - 3%				
Hope	-	42.12	17.31	15.73
Westbury	0.51	0.40	-0.05	-0.32
Northfleet	0.79	-0.58	-0.14	-0.52
Cauldon	2.09	-0.38	-1.49	-1.42
Weardale	[illegible]	[illegible]		

	Delta E	L*	A*	B*
Marshalls Concrete Blocks : Dry		**Minolta 310**		
Hope Cement				
YB3100 at 2%	-	50.85	1.75	18.42
3%	-	51.33	2.03	21.46
4%	-	51.56	2.41	23.75
5%	-	50.14	3.17	25.79
6%	-	52.21	3.11	26.99
7%	-	52.57	3.36	27.88
YB3100 @ 2%	-	50.85	1.75	18.42
3%	3.09	0.48	0.28	3.04
4%	5.41	0.71	0.66	5.33
5%	7.53	-0.71	1.42	7.37
6%	8.78	1.36	1.36	8.57
7%	9.74	1.72	1.61	9.46

TABLE 4

	Delta E	L*	A*	B*
Marshalls Concrete Blocks : Dry		**Minolta 310**		
Hope Cement				
RB2500 at 2%	-	43.74	15.25	14.60
3%	-	42.49	17.74	16.05
4%	-	41.80	19.92	18.03
5%	-	40.71	20.97	18.42
6%	-	40.20	21.79	18.68
7%	-	40.04	22.25	19.50
RB2500 at 2%	-	43.74	15.25	14.60
3%	3.14	-1.25	2.49	1.45
4%	6.11	-1.94	4.67	3.43
5%	7.51	-3.03	5.72	3.82
6%	8.48	-3.54	6.54	4.08
7%	9.31	-3.70	7.00	4.90

TABLE 5

Marshalls Concrete Blocks : Dry

Minolta 310

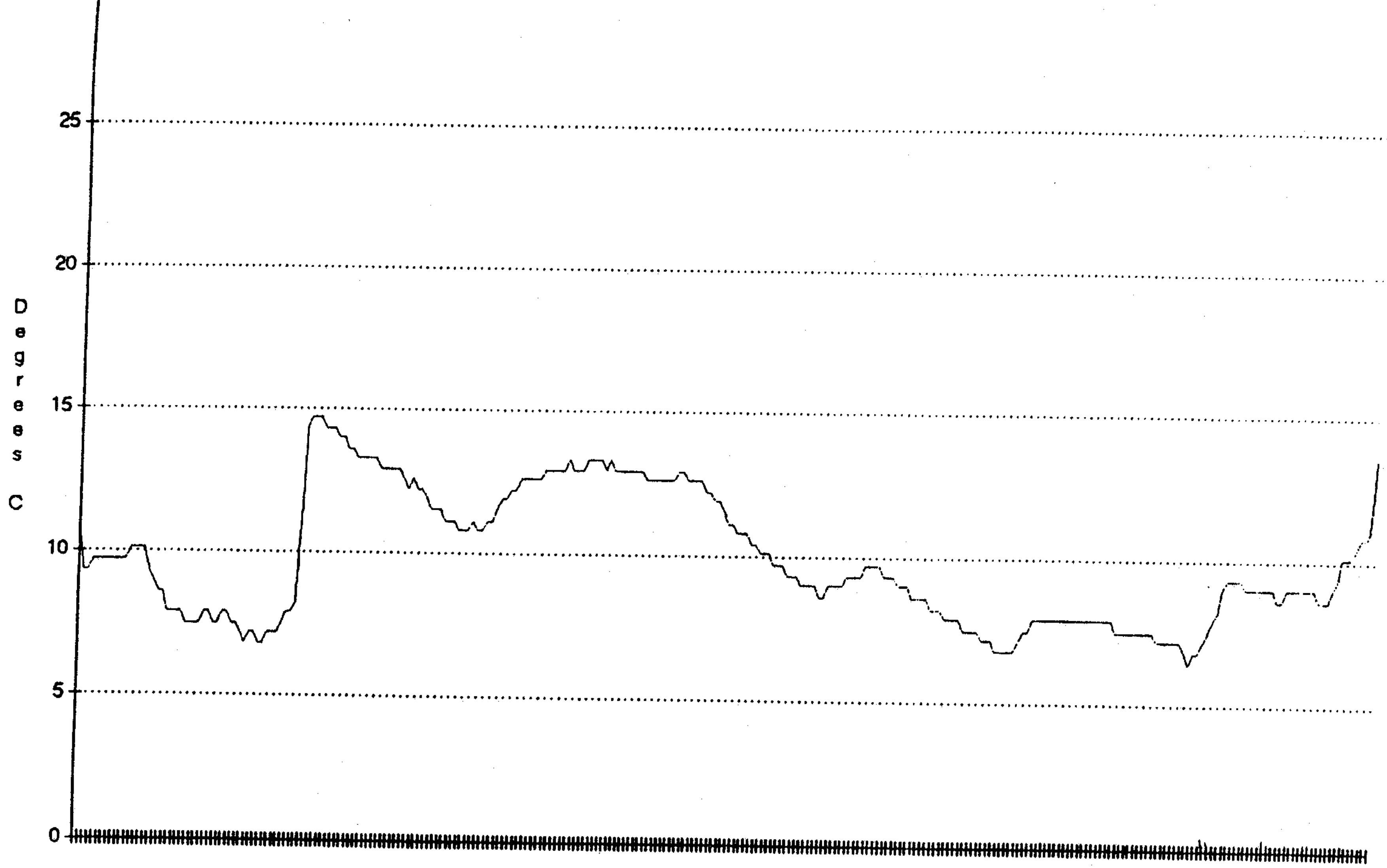
Hope Cement : YB310 at 3%

		Delta E	L*	A*	B*
Water	100%	-	51.44	2.11	22.06
	90%	-	50.34	2.19	21.42
	110%	-	51.75	2.12	22.90
Water	100%	-	51.44	2.11	22.06
	90%	1.27	-1.10	0.08	-0.64
	110%	0.89	0.31	0.01	0.84

Table 6

Westbury Cement : YB3100 at 3%

	Delta E	L*	A*	B*
100% of Grey OPC	-	51.71	1.80	20.28
PFA 1 : L.O.I-3%	-	52.11	1.34	18.65
PFA 2 : L.O.I-5%	-	50.88	1.02	17.76
Slag 1: C.M.S.C.	-	53.89	2.06	22.42
Slag 2		52.88	2.09	22.05
100% Grey O.P.C.	-	51.71	1.80	20.28
PFA 1 : L.O.I-3%	1.74	0.40	-0.46	-1.63
PFA 2 : L.O.I-5%	2.76	-0.83	-0.78	-2.52
Slag 1: C.M.S.C.	3.06	2.18	0.26	2.14
Slag 2	2.51	1.77	0.29	1.77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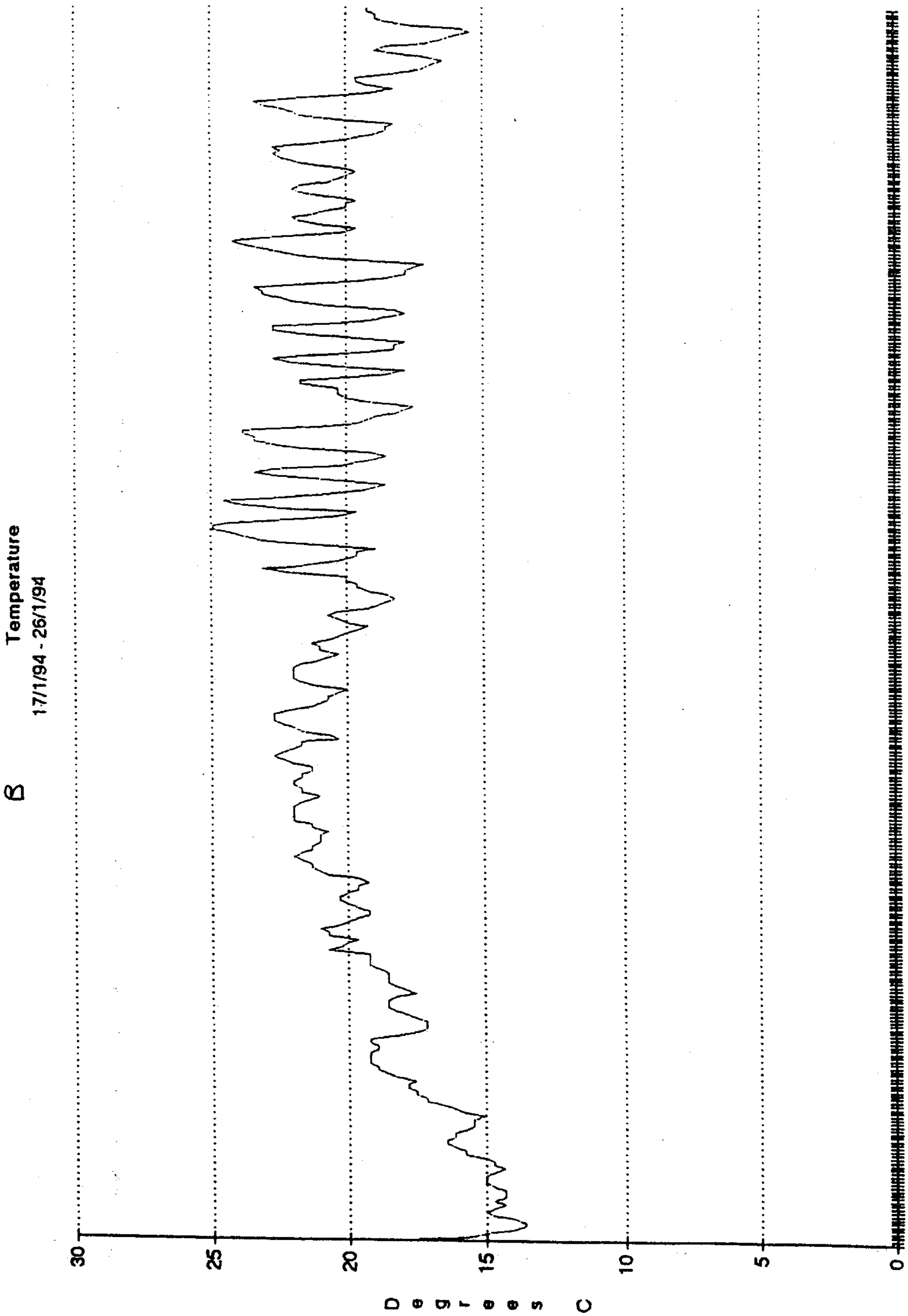
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