Treatments of Recycled Pulps from Old Corrugated Containers. Part II. The Effects of Boron Compounds on Strength Properties

7 8 **ABSTRACT**

9 The selected boron compounds used in this study exhibit a more moderate reduction 10 on burst strength, even though they may only limited improvements in other properties. However, at the fifth recycled stage, guite high burst strength values observed with at both 11 selected boron treatment conditions that approximately 32.31% and 35.94% higher burst 12 strengths at 5.0% level while 20.32% and 14.06% higher burst strengths at 10% boric acid 13 14 and sodium borohydride level compare to control sample at similar recycling phase. The more less similar trend was also observed for tensile strength properties of test papers. The highest 15 tensile strength (index) of 19.74 Nm/g and tensile stiffness value of 386 kN/m was observed at 16 17 second recycling phase with boric acid. For tensile energy absorption (TEA) properties, only 10% sodium borohydride treated test papers showed higher TEA of 23.25 j/m² compared to 18 19 counterpart control samples (C_2 : 20.60 j/m²).

The paper from secondary fibers has generally considered to be used in corrugated 20 21 cardboard production. For this purpose, Sack Corrugated Test (SCT) and Corrugated Medium Tests were used to determine the strength resistance behaviors. The highest CMT value of 22 23 73.5kN/m was found with first recycling stage of control samples. For boron treated pulps, the 24 highest CMT of 63.3 N was found at 10% boric acid treatment at second recycling phase 25 followed by 5.0% boric acid treatment at second recycling phase, respectively. However, some level improvement of SCT properties was observed at certain level both boric acid and 26 27 sodium borohydride treatment conditions. the highest improvements of SCT of test papers was found with 5.0% boric acid treatment at forth recycling phase that show approximately 28 39.74% improvement compared to control. 29

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Keywords: Old Corrugated Container, recycling, boron compounds, tensile strength, burst
 strength, corrugated medium test,

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35 INTRODUCTION

The multi-stage paper production stages affect the structure of cellulose by both 36 37 chemically and physically [1]. To manufacture paper products from recovered cellulosic fibers (secondary fibers/pulps), the secondary pulp needs to have intrinsic strength and some certain 38 properties. However, it was noted that some of the fillers have removed during recycling, 39 which indicates that papermaking from secondary pulps requires higher fillers [2]. Moreover, 40 41 the cellulose fiber undergoes mechanical and drying cycles during papermaking and causing a very complex phenomenon and has not fully explained yet. These changes have usually 42 43 called hornification that irreversible hydrogen bonding potantial and hydrophilic nature of cellulose fibers [3-7]. In addition, the removing of hemicellulose and lignin from the cell wall 44 during recycling also causes the collapse and negative impact on cellulose structure. In 45 hornificated fibers, the amorphous region has typically reduced to some extent resulting 46 increasing crystalline index with lowering re-wetting propeties of fibers [7-11]. 47

Since environmental concern and protection of natural forestslands for papermaking industry, the recycling of post-consumer paper products has become an

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4 5 6 important issue in worldwide. Hence many technologies and alternative approaches have
 become established regarding waste paper recycling.

A typical paper sheet is a composite material that contains cellulosic fibers, air, fillers and some extraneous materials. However, fiber-fiber bonding is closely associated with fibers contact areas and important parameter for paper strengths [12]. Certain chemicals have been reported to be promote fibre bonding and improve paper properties some level [3, 13-16]. It was proposed by Wistara and Young (1999) that the microstructure of cellulose must be modified to establishing further swelling capacity. Moreover, hemicelluloses have also important influences in regulating the physical properties of the pulps during recycling [15].

Although some research conducted for pulping of lignocellulosics with boron 59 60 compunds, and valuable restoring effects on pulp properties [17-20], there has not much information available in literature regarding certain boron compounds treatments of secondary 61 pulps and their effects on paper properties. A systematic approach have carried out with boric 62 acid and sodium borohydride on recycled old orrugated containers (OCC) substrate to 63 64 determine clear effects on recycling approach and chosen methods. In the first part of this study, 'Treatments of Recycled Pulps from Old Corrugated Containers. Part I. The Effects of 65 Boron Compounds on Optical and Physical Properties' has already send to "submitted for 66 67 publication". In the second part of this study, it is aimed to study for providing more 68 fundamental understanding of the strength development of recycled fibres from old corrugated container (OCC) fibers. 69

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71 MATERIALS AND METHODS

72 The additive and treatment free recycled pulps from old corrugated containers were 73 supplied from a commercially operated paper recycling plant, located in Istanbul, Turkey. The 74 purity level of the boron compounds (boric acid and sodium borohydride) used is above 95%. 75 The chemicals were supplied directly from the Etibank Borax plant, located in Bandırma, Turkey. The test papers were prepared as 120 g/m² (typical level for OCC manufactured 76 77 papers) accordance with Tappi Standards (T-202 and T-205). The detailed information on 78 boron compounds, experimental recycling procedures for treatment of OCC substrate and 79 related similar informations have already given in first part of this study.

80 The standard paper strength tests were applied. These involves determination of tensile (T-494) and burst (T-403), strengths. Sack Crushing Strength Test or Short 81 Compression Test (SCT) that is is indicates internal compression resistance of paper fibres 82 and suitable for fluting in the middle layer of the cardboards, was applied on sheets 83 84 accordance with ISO 9895 standard. The SCT properties of papers are expressed in Kilonewtons/Meter (kN/m).The Corrugating Medium Test (CMT) was also conducted on hand 85 sheets followed DIN EN ISO 7263 standard. The CMT determines the flat crush resistance of 86 87 corrugating papers and made on laboratory corrugated samples for describing the usability for fluting. CMT is a way of estimating the crush resistance of corrugated board manufactured 88 with those papers. The CMT is expressed in Newtons (N). Both SCT and CMT tests have 89 used after forming corrugated paper forms, and usually applied on corrugated papers 90 91 alternatively to each other.

92 While many combinations were utilized during recycling procedure of cellulose 93 fibers, some code number and abbreviations were established throughout the study given in 94 Figures and Tables. These are: C: Control, Bx: Boric acid; NaB: Sodium borohydride; 5 and 95 10: chemical concentration %, weight/weight; 1, 2,3,4, and 5: recycling number.

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100 **RESULTS AND DISCUSSION**

The burst strength values of the test papers produced from the control and treated pulps are given comparatively in Table 1. It has realized that the burst strengths of control papers have increased in the first two recycling steps. Then, it has showed a downward trend in further recycling operations. The similar results have also been observed with sodium borohydride and boric acid treated pulps.

However, in general, the burst strength values of sodium borohydride and boric acid 106 107 treated pulps show about 3.22% to 20.43% lower than the control samples up to fourth recycling steps. Interestingly, at the fifth recycled phase, guite high burst strength values 108 109 observed that approximately 32.31% and 35.94% higher at 5.0% concentration while 20.32% 110 and 14.06% higher burst strengths at 10% concentration in comparison to control sample at similar recycling phase. It is important to note that selected boron compounds used in this 111 study exhibit a more moderate reduction on burst strength, even though they may only limited 112 113 improvements in other recycling phases.

Sample	Burst strength (kPa)	Burst index (kPa m²/g)	% Change (from former treatment)	% Change (from control)
C ₁	119	0.95	0.0	0.0
C ₂	118	1.07	8.42	0.0
C ₃	98	0.88	-17.75	0.0
C ₄	102	0.93	5.68	0.0
C 5	70	0.64	-31.18	0.0
5NaB₁	95	0.86	0.0	-9.47
5NaB₂	115	0.92	6.97	-14.10
5NaB₃	92	0.84	-8.69	-4.54
5NaB₄	99	0.90	0.71	-3.22
5NaB₅	87	0.85	-5.56	32.31
10NaB ₁	101	0.81	0.0	-14.73
10NaB ₂	98	0.89	9.87	-16.82
10NaB₃	84	0.78	-12.36	-11.36
10NaB ₄	85	0.83	6.41	-10.80
10NaB₅	68	0.77	-16.87	20.32
5 Bx 1	104	0.83	0,.0	-12.63
5Bx ₂	119	1.08	30.12	0.93
5Bx₃	93	0.82	-24.07	-6.81
5 Bx 4	93	0.86	4.87	-7.53
5Bx₅	104	0.87	1.16	35.94
10Bx ₁	114	0.91	0.0	-4.21
10Bx ₂	110	1.0	9.89	-5.61
10Bx₃	88	0.80	-20.0	-9.09
10Bx ₄	81	0.74	-7.50	-20.43
10Bx₅	66	0.73	-1.35	14.06

Table 1. Burst strength properties of papers made from recycled OCC pulps

Figures 1 and 2 show the effects of boron compounds concentration in recycling stages on 114 burst strength properties of hand sheets. It has been observed that the increasing sodium 115 borohydride concentration at higher recycling phase has no positive effects while at lower 116 recycling number (up to two) and sodium borohydride concentration shown to improving burst 117 strengths of sheets (Figure 3). Like sodium borohydride treatments, lower recycling phase 118 (up to two) but in both level boric acid concentration have increasing effects on burst strengths 119 of sheets (Figure 4). ilncreasing recycling phase beyond second recycling phase have not 120 effective for improving burst strengths of papers made from selectec boron treated recycled 121 OCC pulps. 122



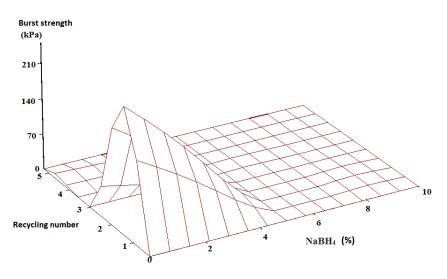
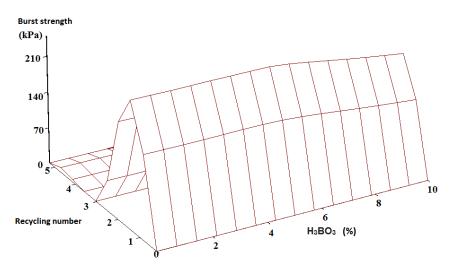


Figure 1. The effects of sodium borohydride concentration and recycling phase on burst strengths of papers



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Figure 2. The effects of boric acid concentration and recycling phase on burst strengths of papers

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In Table 2 the tensile strengths properties of the test papers are given comparatively.
 In general, the tensile properties (index) of control samples did not change much and even
 decreased only by 1.20% to 5.79%, continuously recycling procedure. It is important to note

that no any improvements was observed with sodium borohydride treated pulps regardsless of concentration and recycling phase, except 10% treatment conditions at second recycling stage (10NaB₂) that shows only 3.23% improvement in comparison to control samples.

For boric acid treatments, except in 5.0% conditions at first recycling stage (5Bx₁), 2.69 to 8.34% improvements of tensile strengths were observed compare to counterpart control samples. The highest tensile index of 19.74 Nm/g was observed at second recycling stage (5Bx₂).

140 Stretch is usually reported percentage of elongation. As seen in Table 2, marginally changes were observed regarding stretchs of papers. The changes occurs only in marginal 141 limits. However, tensile stiffness is the ratio of tensile force per unit width to tensile strain 142 143 within the elastic region of the tensile-strain relations. The highest tensile stiffness value of 386 kN/m was observed with 5.0% boric acid treatment at fifth recycling phase that is the only 144 higher value for boron treated pulps regardless of recycling phase, than counterpart control 145 samples. Tensile energy absorption (TEA) is the work done when a specimen is stressed to 146 147 rupture in tension under prescribed conditions. It is expressed as energy per unit area (test span x width) of test specimen. For sodium borohydride treatments of secondary pulps, only 148 10% treated pulps at second recycling phase (10NaB₂) show higher TEA of 23.25 J/m² 149 150 compared to counterpart control samples (C_2 : 20.60 J/m²). It is important to note that boric 151 acid seems to be effective only at 5.0% concentration phase (except first recycling stage).

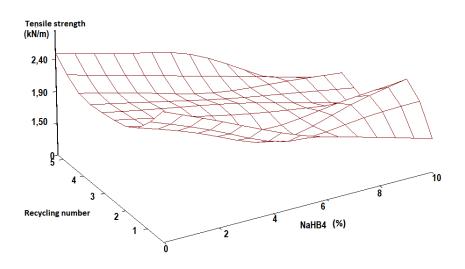
From the results observed in Table 2, it can be summarized that treatment of OCC secondary fibers with both boron compounds at 5.0% treatment levels have some restoring/improving effects on the tensile strength values at certain treatment phases.

Sample	Tensile strength (kN/m)	Stretch (%)	TEA (J/m²)	Tensile stiffness (kN/m)	Tensile index (Nm/g)
C ₁	2.40	1.69	31.20	356	19.34
C ₂	2.15	1.34	20.60	341	18.22
C ₃	2.09	1.28	19.15	313	18.0
C ₄	2.08	1.27	16.10	255	18.26
C 5	2.24	1.21	18.15	328	18.98
5NaB₁	2.02	1.88	26.75	269	16.10
5NaB₂	1.85	1.52	20.40	273	16.67
5NaB₃	1.93	1.25	17.05	272	17.79
5NaB ₄	1.87	1.27	16.10	254	17.32
5NaB₅	2.02	1.29	17.85	291	18.53
10NaB ₁	1.77	1.96	25.0	212	14.71
10NaB ₂	2.05	1.59	23.25	274	18.81
10NaB₃	1.72	1.20	14.10	259	17.73
10NaB ₄	1.80	1.80	16.20	257	17.39
10NaB₅	1.54	0.95	10.33	266	17.50
5 Bx 1	1.93	1.72	23.25	254	16.69
5 Bx ₂	2.23	1.45	22.90	302	19.74
5Bx₃	2.13	1.32	19.50	290	18.85

Table 2. Tensile strength properties of papers made from recycled OCC pulps

5 Bx 4	2.16	1.29	19.80	296	18.94
5Bx₅	2.30	1.14	19.15	386	19.49
10Bx1	1.96	1.71	24.0	253	15.68
10Bx ₂	1.93	1.09	14.83	289	17.31
10Bx₃	1.97	1.42	19.25	267	18.41
10Bx ₄	1.74	1.20	14.20	253	16.57
10Bx₅	1.42	1.10	10.71	228	13.40

Figures 3 and 4 show the combine effects of sodium borohydride and boric acid concentration during recycling phases on tensile strength properties of test papers. It has been observed that the increasing sodium borohydride concentration at low recycling phase marginally improving effects (**Figure 3**). In contrast to sodium borohydride, low level of boric acid concentration and higher recycling phase positive affects tensile strengths of sheets (**Figure 4**). In this sense, increasing boric acid contcentration to 10% up to third recycling phase not effective for improving tensile strengths of papers.



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Figure 3. The effects of sodium borohydride concentration and recycling phase on tensile strengths of papers

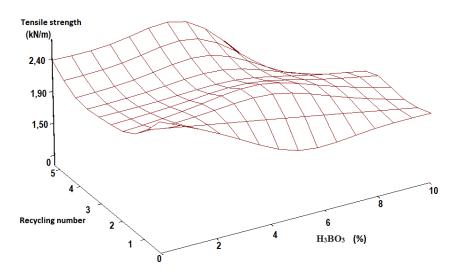


Figure 4. The effects of boric acid concentration and recycling phase on tensile strengths of papers

The Corrugate Medium Test (CMT) values of the test papers are given in Table 3. It can be seen that there is not certain restoring trend realized for the CMT values of test papers. It seems to selected boron compounds have not positively affected the CMT of papers. The highest CMT value of 73.5 N was found after first recycling stage of control samples. However, for boron treated pulps, the highest CMT of 63.3 N was found at 10% boric acid treatment at second recycling phase (10Bx₂) followed by 5.0% boric acid treatment at second recycling phase (5Bx₂), respectively.

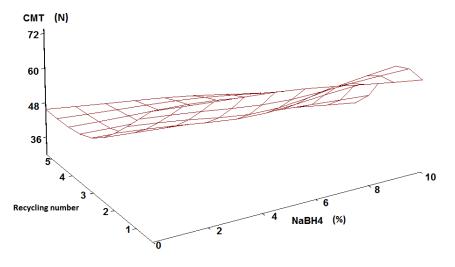
 Table 3. Corrugated Medium (CMT) strength properties of papers made from recycled OCC pulps

Sample	СМТ	Change	Change
	(N)	(%, from former stage)	(%, from control)
C ₁	73.5	0.0	0.0
C ₂	60.7	-17.41	0.0
C ₃	50.0	-17.62	0.0
C ₄	46.0	-8.0	0.0
C ₅	45.7	-0.06	0.0
5NaB ₁	69.3	0.0	-5.71
5NaB ₂	54.3	-21.64	-10.54
5NaB₃	46.7	-13.99	-6.60
5NaB ₄	43.7	-6.2	-5.00
5NaB₅	39.0	-10.76	-14.66
10NaB ₁	61.7	0.0	-16.05
10NaB ₂	59.0	-4.38	-2.80
10NaB₃	40.1	-3.03	-19.98
10NaB ₄	37.0	-7.73	-19.56
10NaB₅	29.7	-1.72	-35.01

5 Bx 1	63.3	0.0	-13.54
5 Bx 2	62.3	-1.58	2.63
5Bx ₃	43.3	-30.49	-13.40
5 Bx 4	41.7	-12.70	-7.17
5 Bx ₅	36.0	-21.21	-21.22
10Bx ₁	60.7	0.0	-17.41
10Bx ₂	63.3	5.43	4.28
10Bx₃	43.3	-31.59	-13.40
10Bx4	39.0	-9.90	-15.21
10Bx₅	29.7	-23.84	-35.01

Figures 5 and 6 show the effects of boron compounds of sodium borohydride and boric acid in recycling phases on CMT properties of test papers. It has been observed that the increasing sodium borohydride concentration do not influence on CMT values while increasing reycling number negatively affects the test papers. Interestingly, more less similar trend was also observed in case of boric acid treatment conditions as seen in Figure 6.





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Figure 5. The effects of sodium borohydride concentration and recycling phase on CMT properties of papers

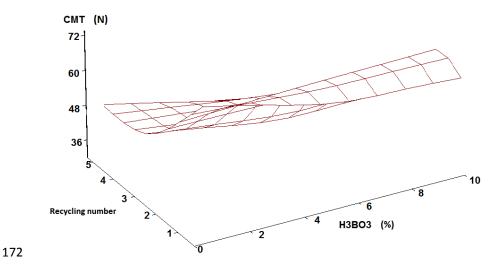


Figure 6. The effects of boric acid concentration and recycling phase on CMT properties of papers

The paper from secondary fibers has generally considered to be used in corrugated 174 175 cardboard production. For this purpose, Sack Corrugated Test (SCT) is used to determine the surface crush strength resistance behaviors. In this test, the content of paper is more sensitive 176 than fiber content as compared to conventional testing methods. In Table 4, the SCT values of 177 the test papers produced from the treated secondary fibers with the control and boron 178 compounds are given comparatively. As seen in Table 4, the SCT properties of the (control) 179 papers showed a steady decline as the recycling stage increased. It is very complicated to 180 181 interpret the data presented in Table 4. However, some level improvement of SCT properties was observed at certain level of samples treated by both boric acid and sodium 182 borohydride. However, the highest SCT value of 1.18 kN/m was found for control sample 183 (C1). The highest improvement of SCT of test papers under treatment conditions with 5% 184 boric 5.0% boric acid at forth recycling phase (5Bx₄) that shows approx. 39.74% improvement 185 as compared to control samples (C4: 0.78 kN/m vs 5Bx4: 1.09 kN/m), followed 16.44% 186 187 improvement by fifth recycling phase at same boric acid concentration.

Treatme	SCT	% Change	% Change
nt	(kN/m)	(from former treatment)	(from control)
C 1	1.18	0.0	0.0
C ₂	1.16	-1.72	0.0
C ₃	1.09	-7.62	0.0
C ₄	0.78	-28.44	0.0
C ₅	0.73	-0.64	0.0
5NaB₁	0.96	0,0	-17.24
5NaB₂	0.88	-9.38	-26.27
5NaB₃	0.87	-1.14	-19.27
5NaB ₄	0.78	-11.36	0.0
5NaB₅	0.92	17.94	8.00

Table 4. SCT strength properties of papers made from recycled OCC pulps

10NaB ₁	0.90	0.0	-22.41
10NaB ₂	1.09	21.11	-7.63
10NaB₃	0.92	-15.59	-15.59
10NaB ₄	0.84	-8.69	7.69
10NaB₅	0.67	-20.24	-8.21
5 Bx 1	0.99	0.0	-14.65
5Bx ₂	1.15	16.16	-2.54
5 Bx 3	1.0	-13.04	-8.26
5Bx4	1.09	8.26	39.74
5Bx₅	0.85	-22.02	16.44
10Bx1	0.98	0.0	-15.51
10Bx ₂	1.13	15.31	-4.23
10Bx ₃	0.92	-18.58	-15.59
10Bx4	0.82	-10.87	-5.13
10Bx₅	0.66	-19.51	-9.59

The results given in Table 4 were used to interpret selected boron compounds and recycling phase effects on SCT properties of tested papers. Hence, sodium borohydride and boric acid effects during recycling stages effects on SCT properties presented in Figure 7 and 8, respectively.

193 It can be seen that middle level of recycling (up to third) with 10% sodium 194 borohydride has some improving effects on SCT properties (Figure 7). However, treatment of 195 secondary OCC fibers with boric acid was found to have the only positive effect on the SCT 196 properties at low concentration (5.0%) and at middle level recycling stages (up to third) (Figure 197 8).

198 In general, it has been observed that the increase in recycle number and selected 199 boron content concentrations have usually negative impact on the SCT properties of the test 200 papers, but the SCT value changes were found to be within marginal levels for certain 201 treatment conditions (see in Table 4)

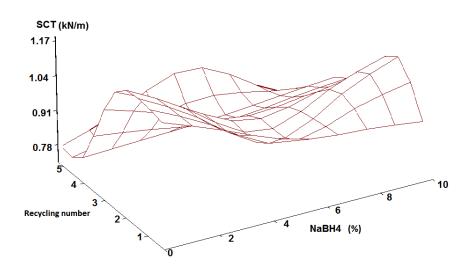
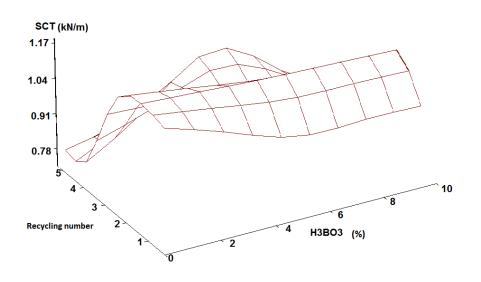


Figure 7. The effects of sodium borohydride concentration and recycling phase on SCT properties of papers

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Figure 8. The effects of boric acid concentration and recycling phase on SCT properties of papers

Wistara et al. (1999) reported that the recycling affects lowering surface energy of 205 206 cellulosic fibers. This hypothesis has been suggested that the disruption of hemicelluloses may occur during recycling of cellulose. They have proposed that some compounds could be 207 208 capable oxidizing fiber surfaces resulting increasing carboxylic and OH groups on the surface of the fibers during recycling. These clearly affect substitution of -OH groups and resulting 209 further swelling and, improve physical properties of sheets [15]. In our study, there has only 210 marginal improvements of paper strengths was observed while some properties have been 211 found to be restore at certain boron compounds treatment conditions. 212

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214 CONCLUSIONS

The corrugated container manufaturing is an important sub parts of papermaking 215 216 industry. This is because of wide utilization of these products in packaging and transportation 217 needs other consumer products. Thereby, the recycling of these products has important issue 218 and to modify on similar products that they usually re-manufactured from those recycled 219 fibers. The selected boron treatments of the recovered secondary OCC pulps are aimed to 220 improve some strength propertie of sheets made. Although the use of boric acid and sodium 221 borohydride during recycling of OCC pulps as treatment agents shows some variables and limited restoring/improving results on some selected strength properties, the results have 222 223 found in this study might be a basement for further studies.

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