4-1974

No-Sulfur Semi-Chemical Pulping with Na_2CO_3 and NaOH

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by

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A Thesis Submitted To The Faculty
of the Department of Paper Science & Engineering
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan
April, 1974

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ABSTRACT

Na_2CO_3/NaOH cooking liquors were evaluated as possible pulping agents for the production of semichemical pulp for use in corrguating medium. Optimum ratios of Na_2CO_3/NaOH were found to be 2/1 to 4/1. Pulp produced with ratios within these figures were equal to tensile and concora and higher in yield when compared to NSSC pulp made at the same temperature, time and Na_2O/chip ratio. By increasing either the time or the Na_2O, higher tensile and concora tests were obtained but with a slight sacrifice in yield. Na_2CO_3/NaOH pulps are more resistant to refining than NSSC pulps made under comparable conditions and in some cases required more than twice the beating time to reach target Canadian Standard Freeness tests.

HISTORICAL BACKGROUND

The neutral sulfite semi-chemical process was first developed in the 1920's and has changed little in the past forty years. In the late 1950's, the institute recovery process was developed which allowed chemical reuse and reduced liquor discharge problems. An unfortunate side effect of this process is the odor produced from H_2S and other sulfur compounds (1). With the recent emphasis on air pollution, the sulfur free pulping process would be desirable.

In 1959 Freedman reported on two stage soda pulping of hardwoods using 10% Na_2CO_3 in the primary hydrolysis followed by 14 to 19% NaOH in the second stage. He found that pulp properties were in some cases superior to kraft pulps (2).

In 1965, Winczakiewiez and Kaszynska reported on laboratory pulping of Polish hardwoods with Na_2CO_3. Six percent Na_2CO_3 was found to be best with 2.5 hours to heat to 170°C followed by 30 minutes reaction time at this temperature. Birch chips gave pulp of 85% yield and a concora of 47 while Beech chips gave an 88% yield and a concora of 51, (425 ml CSF, 130 g/m^2). NSSC pulping to 70 and 71% yield gave concoras of 56 and 57 for Beech and Birch chips respectively (3). They also pointed out that a kraft mill recovery system could use the Na_2CO_3 as soda-makeup (3). Moore

and Saul suggested that an independent semi-chem mill could use the Zimpro combustion process for recovery (4).

It was recently reported however, that Na_2CO_3 pulp is $5/ton more expensive than NSSC pulp (5).

In 1972, Yerger reported results of semi-chemical pulping using only minor amounts of $Na2SO_3$. Liquor containing 3.0% Na_2CO_3, 1.35% NaOH, 0.45% Na_2SO_3, and trace quantities of Na_2S produced a concora of 50 at 76.2% yield. A liquor with 2.25% Na_2SO_3, 2.0% Na_2CO_3, and 0.13% NaOH gave the same concora at 74.3% yield (6).

Worster suggested that this small amount of Na_2SO_3 could probably be eliminated without difficulty and noted that recovery of spent liquor would be the same as with Na_2CO_3 except that part of the soda green liquor would have to be recausticized at an additional cost (7).

In 1957, Owens Illinois began research to find a non-sulfur process as the only practical route around, the odor problems associated with the Institute Recovery Process. They first developed a process which reduced the quantity of sulfur used by 80%. Now however, they are using an entirely sulfur free process invented by John Kennedy, Byron Dillard and R.J. Gilmer (1).

While no specific details on the process have been released, it has been stated that the process uses sodium compounds which are readily available commercially and which can be recovered for reuse. O-I reports 10-20% reduction in chemical usage and $1-2/

ton chemical savings (1).

They state that only minor changes in the pulping conditions are required and that no major changes in the time-temperature relationship (which might affect capacities) were observed. According to O-I, all species of hardwoods currently pulped using the sulfite semi-chemical process can be pulped by the process (1).

Refining was found to be uneffected and no startup problems were encountered. Corrugating mediums of at least equal quality to conventional NSSC medians are currently being produced at both the Big Island and the Tomahawk Wisconsin mills. The machines have set several production records with the new pulp, and corrugaotrs operators using their medium report excellent results and some speed increases. The only difference is a slightly darker color (1). Odor and soot problems have been completely eliminated (1, 9), "a slight odor of cooking wood" (8) remaining. No increases in water pollution loads have been noted (1).

Westvaco's Covington mill has been operating a no-sulfur process since September, 1971. Existing equipment has been successfully converted to non-sulfur pulping and no conversion problems were encountered. Westvaco reports a 5-10% savings when using its no-sulfur process (10).

The system can be operated separately or in conjunction with a kraft mill and no limitations were imposed on the ratio of kraft

to semi-chem. Both Owens Illinois and Westvaco have applied for patents on their processes and have agreed to license them.

DEFINITION OF THE PROBLEM

This study evaluates combinations of Na_2CO_3 and NaOH as pulping agents for the production of semi-chemical pulps. The work was done in three parts, these were:

1. Using a 2/1 ratio of Na_2CO_3 to NaOH at variable chemical concentrations and cooking times.
2. Finding the optimum ratio of Na_2CO_3 to NaOH.
3. Determining pulp properties from various special cooks.

EXPERIMENTAL

All cooks were made in a laboratory bomb digester at a constant liquor to O.D. wood ratio of 3/1. 60% Oak and 40% Soft Maple chips from single trees were used. The chips used contained no bark and were approximately 5/8 inch long. The temperature of the cooks was 170°C (338°F) with five minutes allowed for the bombs to reach cooking temperature.

All the cooked chips were defibered in the laboratory Bauer Single Disk refiner at 65°C (150°F) and 3% consistency. The defibered pulps were washed carefully for yield determination and beater runs were made in a Valley Beater using TAPPI Standard conditions except that 25% less weight was used to preserve tear strength and magnify differences in beating times. Noble and Wood handsheets were made at 26.0 lbs/1000 $ft.^2$.

Phase I

In the first phase, the objective was to determine the properties of pulps produced using a 2/1 ratio of Na_2CO_3 to NaOH.* 7, 10, and 13% Na_2O were used at 20, 40 and 60 minute cooking times. In addition, two NSSC controls were made.

* All chemicals reported as Na_2O equivalents.

Results and Discussion

Table I summarizes the properties of these pulps. All results are listed at 200 ml CSF.

1. Concora** - As a whole, concora is better at higher chemical concentrations and longer cooking times. Concora tests equal or superior to the neutral sulfite controls were achieved over a wide experimental range.
2. Tensile - Tensile tests were generally somewhat lower in the no-sulfur pulps except at the higher chemical concentrations and longer cooking times. Tensile tests did not appear to be strongly dependent on yield in the no-sulfur handsheets.
3. Tear - The best tear tests were obtained at the longest cooking times and the highest chemical concentrations. Tear tests were similar to or higher than the neutral sulfite controls except at the lowest chemical usage and shortest cooking times.
4. Mullen - Mullen tests on the no-sulfur pulps were generally about 20% lower than the controls.

** The concora test involves fluting a paper strip, laminating it to a tape backing and then measuring the force required to crush the flutes. The Concora test is generally the most critical quality test for corrugating median.

Mullen tests improved with increasing cooking time and chemical concentration and was similar to the control at 13% Na_2O and 60 minutes cooking time.

5. TEA - Tensile Energy Absorption* (TEA) of the no-sulfur pulps were similar to or higher than the NSSC controls. Highest TEA's (related to runnability) were obtained at longer cooking times and at the higher chemical concentrations.
6. Yields - No-sulfur pulps have 2-5% higher yields than the NSSC pulps for the same pulp properties.
7. Beating Times - Beating times of the no-sulfur pulps were significantly higher than the NSSC controls. This would indicate that no-sulfur pulps may require more horsepower applied at the refiners. The difficulty in fibrillation of this fiber may explain the lower mullen tests of the no-sulfur pulps.
8. Some caliper variations were found in the handsheets made with different pulps. These variations appear to have some effect on concora - see appendix.

* TEA - Tensile Energy Absorption is a measure of the area under the Instron Tensile Tester's stress-strain curve. It measures how much energy the sample absorbed before breaking and is related to the "toughness" of a paper sample.

Phase II

The objective of this phase was to determine to optimum ratio of Na_2CO_3 to NaOH. All pulps were made using 10% Na_2O and a 40 minute cooking time. Ratios from 2/1 to 9/1 were evaluated.

Results and Discussion

Table II shows the results of the ratio study. All values were reported at 200 ml CSF.

1. Concora - Concora tests higher than the NSSC control were obtained with ratios of 2/1 to 4/1 with the 4/1 giving the highest concora. At ratios above 4/1, the concora tests were very low. Possibly the NaOH was exhausted during the first part of the cook leaving only Na_2CO_3 for the remainder of the cook. Figure I shows a plot of concora vs Na_2CO_3/NaOH ratio.
2. Tensile - Generally tensile test results were similar to the NSSC control at ratios between 2/1 and 4/1.
3. Tear - Tear values were found to be similar to the NSSC control at ratios between 2/1 and 4/1.
4. Mullen - The mullen tests results generally decreased as the ratio of Na_2CO_3 to NaOH increased. Mullen values were lower than the NSSC control.

5. TEA - Tensile Energy Absorption values of the no-sulfur pulps were higher than the NSSC control except at the 9/1 ratio. No correlation was found between the TEA results and the chemical ratio used.
6. Beating time - No correlation was found between ratio and beating time. The 3/1 pulp had the lowest time of the no-sulfur pulps but beating time for the NSSC control was much lower.

Phase III

The objective of Phase III was to evaluate certain special cooks and to develop ways to reduce the refining time of the no-sulfur pulps.

Experimental

0.2% Triton X-400*, a quatranary ammonium salt surfactant was dissolved in the liquors using surfactants. Surfactant addition was evaluated at chemical ratios of 6/1 and 2/1.

10 lbs/in^2 of oxygen was added to the digester bombs using a 6/1 chemical ratio to evaluate the effect of oxygen on pulp properties. Since O_2 at high temperatures is known to produce pulps of low strength, the cooking temperature was reduced to 125^{o}C.

* Triton X-400 is an aqueous dispersion of stearyl dimethyl benzyl ammonium chloride at 25% solids, (Rohm and Haas Company) used as a softening agent for textiles, etc.

100% NaOH was also evaluated as a pulping agent.

Results and Discussion

Table III summarizes the results of the special cooks.

1. The addition of surfactant produced large increases in concora in the 6/1 Na_2CO_3/NaOH pulp. Surfactant added to the 2/1 cook reduced concora and yield possibly because of over-cooking. Reducing the chemical concentration improved this property somewhat.
2. Surfactant addition tends to increase yield 2-4% but decreases physical properties,* possibly due to the softening of the fiber.
3. Surfactant addition significantly reduced beating time in the Na_2CO_3/NaOH pulps. More work with different surfactants will be required before further conclusions can be drawn.
4. The 6/1 O_2 pulp, while lighter in color, had very poor physical properties.
5. This study shows that 100% NaOH can produce an excellent pulp but at a 5% lower yield and with somewhat higher refining requirements than conventional NSSC pulps.

* Except the tear test.

CONCLUSIONS

1. Na_2CO_3/NaOH pulps can produce pulps of equal or superior quality to NSSC pulps over a wide range of experimental conditions. The best pulp properties were obtained at longer cooking times and higher chemical concentrations. Mullen tests may be slightly lower than conventional NSSC pulps.
2. The no-sulfur pulps have a 2-4% higher yield for the same physical properties as NSSC controls.
3. Refining requirements appear to be much higher for the no-sulfur pulps and may require additional horsepower at the refiners.
4. Quality pulps can be made at ratios between 2/1 and 4/1 with the 4/1 ratio producing the best pulps. At ratios above 4/1, physical properties fall off drastically.
5. Surfactant addition significantly reduced the beating times of the no-sulfur pulps and increased yields 2-4%. The surfactant may improve physical properties i.e., concora at the higher chemical ratios (6/1) but appears to lower them at the 2/1 ratio. More work needs to be done with other surfactants to determine the merit of surfactant addition.
6. Excellent quality pulp can be produced using 100% NaOH but but at a 5% lower yield and with somewhat higher refining requirements

TABLE II

$Na_2CO_3/NaOH$ - RATIO STUDY

10% Na_2O (200 ml CSF)

$Na_2CO_3/NaOH$	2/1	2.3/1	3/1	4/1	6/1	9/1	NSSC CONTROL 9.9% Na_2O
Res. pH	9.1	8.8	8.5	8.7	8.6	8.5	7.6
Yield, %	76.2	74.8	73.9	77.1	74.9	77.1	74.8
Concora, lbs.	67	66	67	69	45	45	65
Tensile, kg.	18.7	13.2	17.3	19.8	12.0	15.2	20.8
Tear	69	78	73	60	84	53	74
Mullen	52	37	48	43	33	27	59
TEA	2.31	1.35	1.85	2.08	1.44	1.07	1.09
Beating Time (Minutes) 600-200 CSF.	98	126	81	92	100	90	58
Caliper	12.0	12.8	11.6	11.6	12.0	12.3	12.8

Figure 1

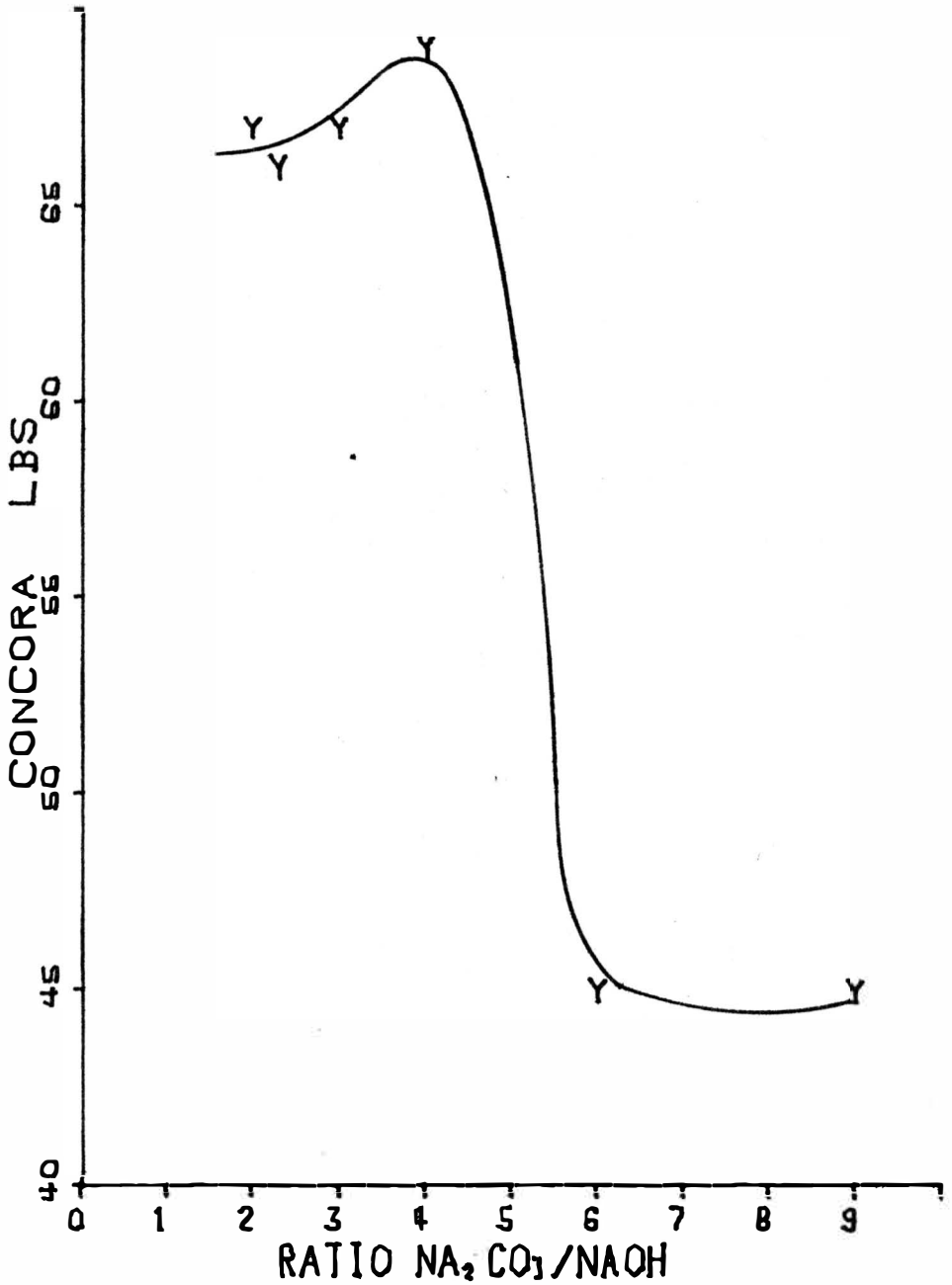

TABLE III

SPECIAL COOKS

Na_2CO_3/NaOH	6/1	6/1 +.2% Surfactant*	6/1+O_2	2/1	2/1 +.2% Surfactant*	2/1 +.2% Surfactant*	100% NaOH	100% NaOH +2% Surfactant*	NSSC Control
%, Na_2O	10	10	10	10	10	7	10	7	9.9
Res. pH	8.6	8.5	8.7	9.1	8.9	7.6	9.8	9.5	7.6
Yield, %	74.9	77.2	82.5	76.2	71.5	76.8	69.5	74.6	74.8
Concora	45	61	39	67	44	53	66	47	65
Tensile	12.0	11.7	8.0	18.7	9.5	12.4	-	11.1	20.8
Tear	84	76	39	69	71	78	90	73	71
Mullen	33	33	15	52	32	37.5	66	31	59
Beating Time (600-200 CSF)	100	91	135	98	54	59	87	88	58
Caliper	12.0	11.7	14.1	12.0	12.1	12.8	10.1	13.5	12.8

* Triton X-400 (25% solids)

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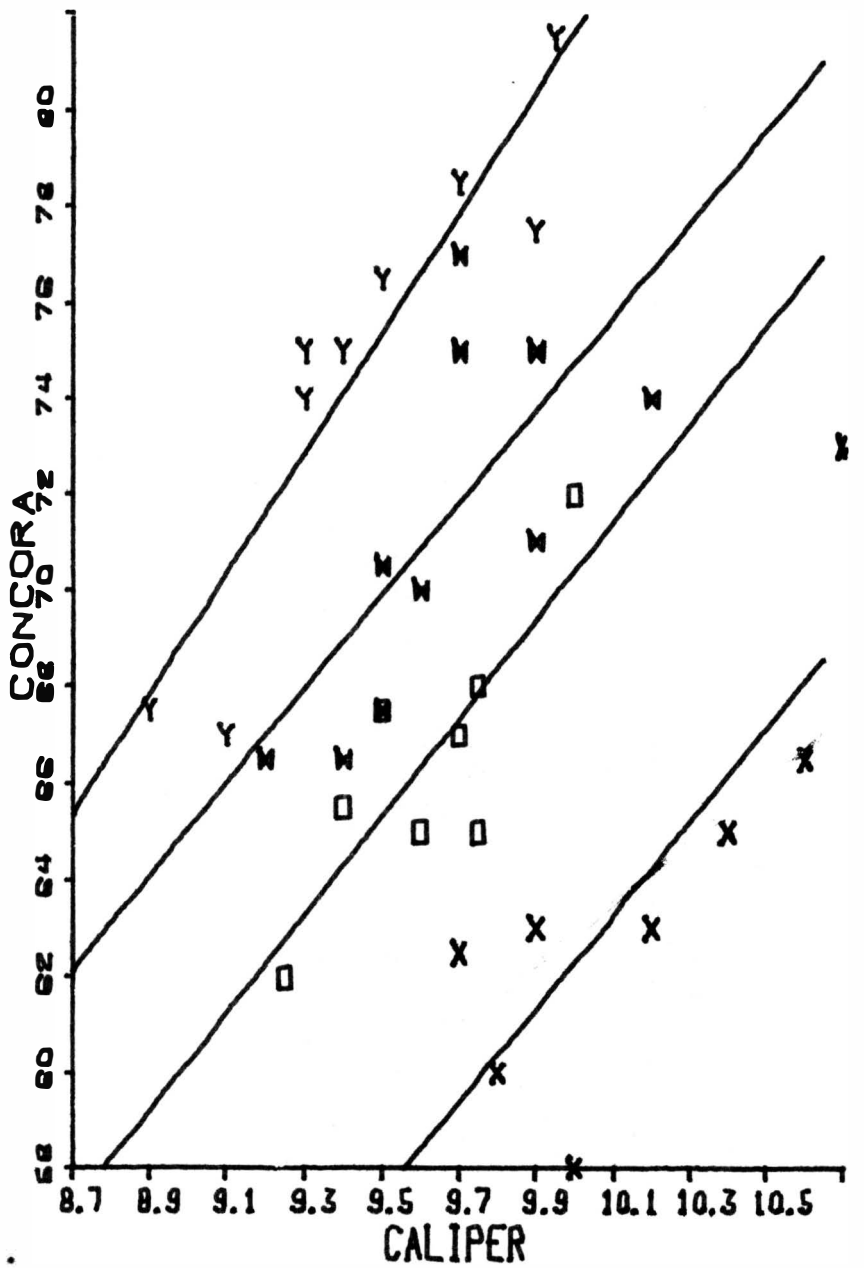
APPENDIX I

Noble and Wood handsheets were made using 2/1 Na_2CO_3/NaOH pulp (10% Na_2O-40 minutes cook time). The sheets were pressed using varying amounts of weight on the Noble and Wood press. The sheets were dryed and conditioned in the conventional manner and paper strips for the concora test were measured for caliper individually.

The figure shows the plots of concora vs caliper for the different press weightings used. The increasing values of concora with increasing press pressure (at the same caliper) indicate that maximum press loading without crushing is desirable and that concora values may vary with small changes in caliper. A calibration curve which takes into account the caliper of the concora strips being tested may reduce paper rejection and improve process control in the mill.


CONCORA
58
60
62
64
66
68
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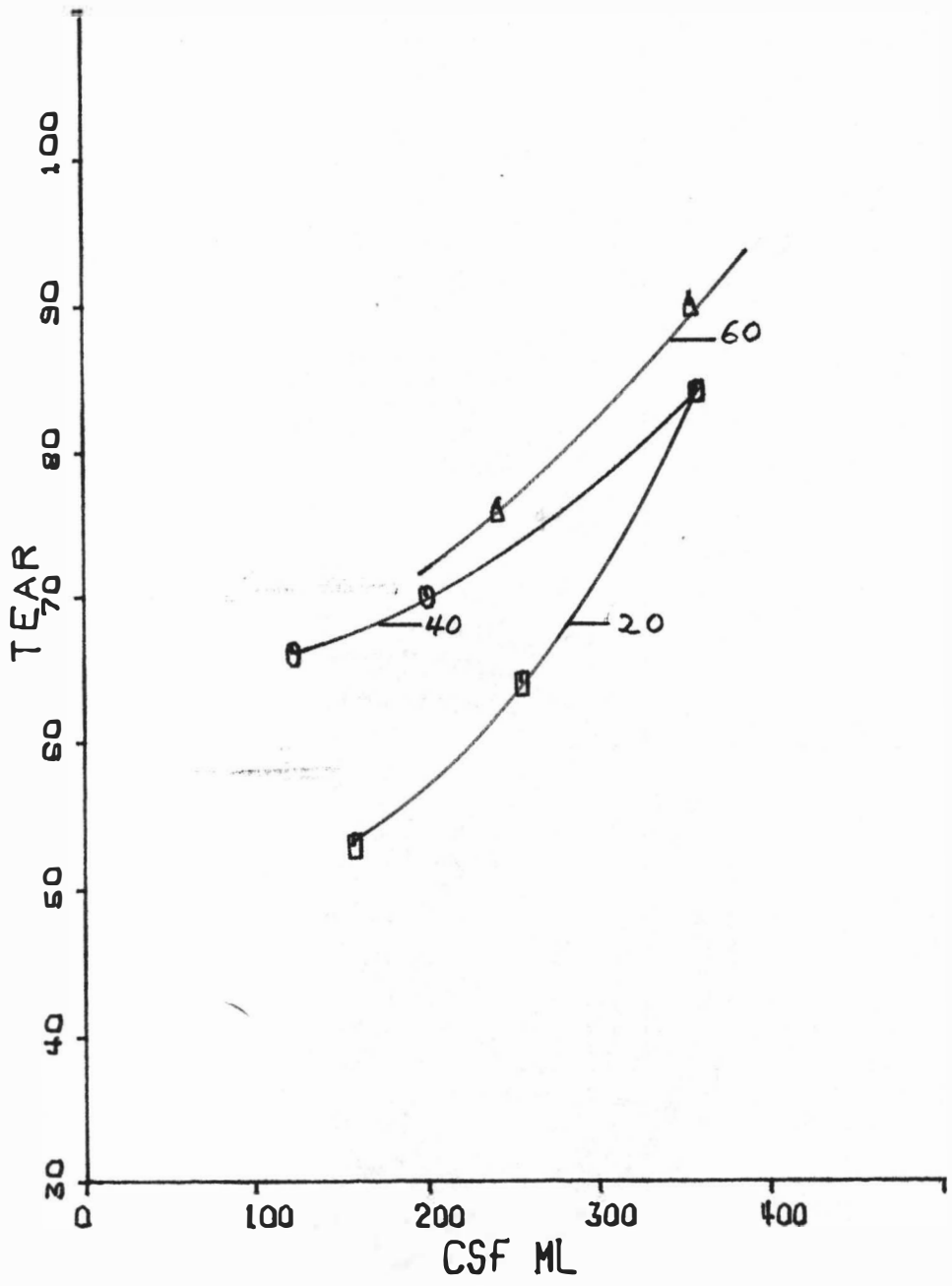
72
74
76
78
80
8.7
8.9
9.1
9.3
9.5
9.7
9.9
10.1
10.3
10.5
CALIPER

APPENDIX II

Phase I - physical properties vs freeness

7% Na_2O-variable time (minutes)



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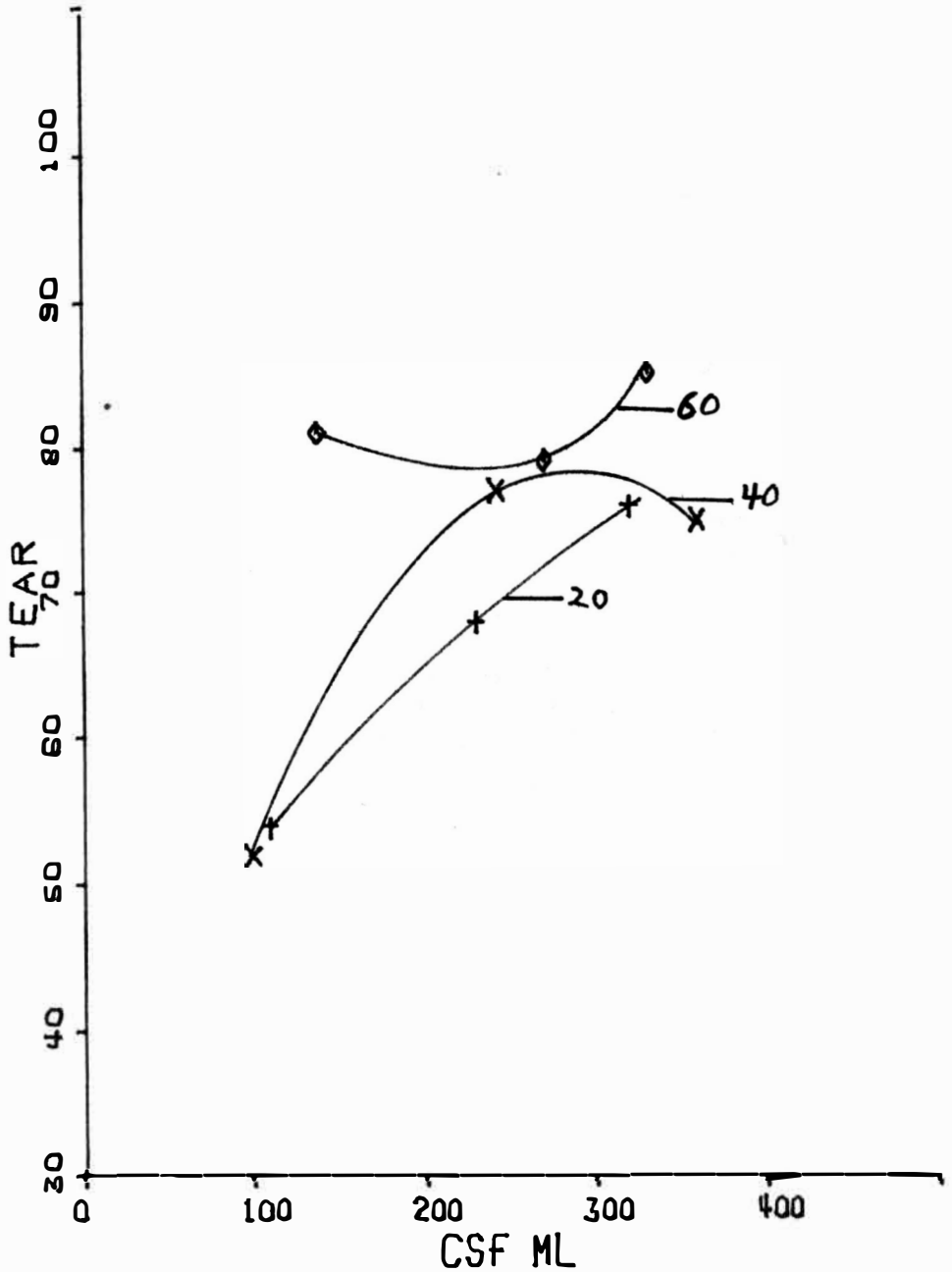

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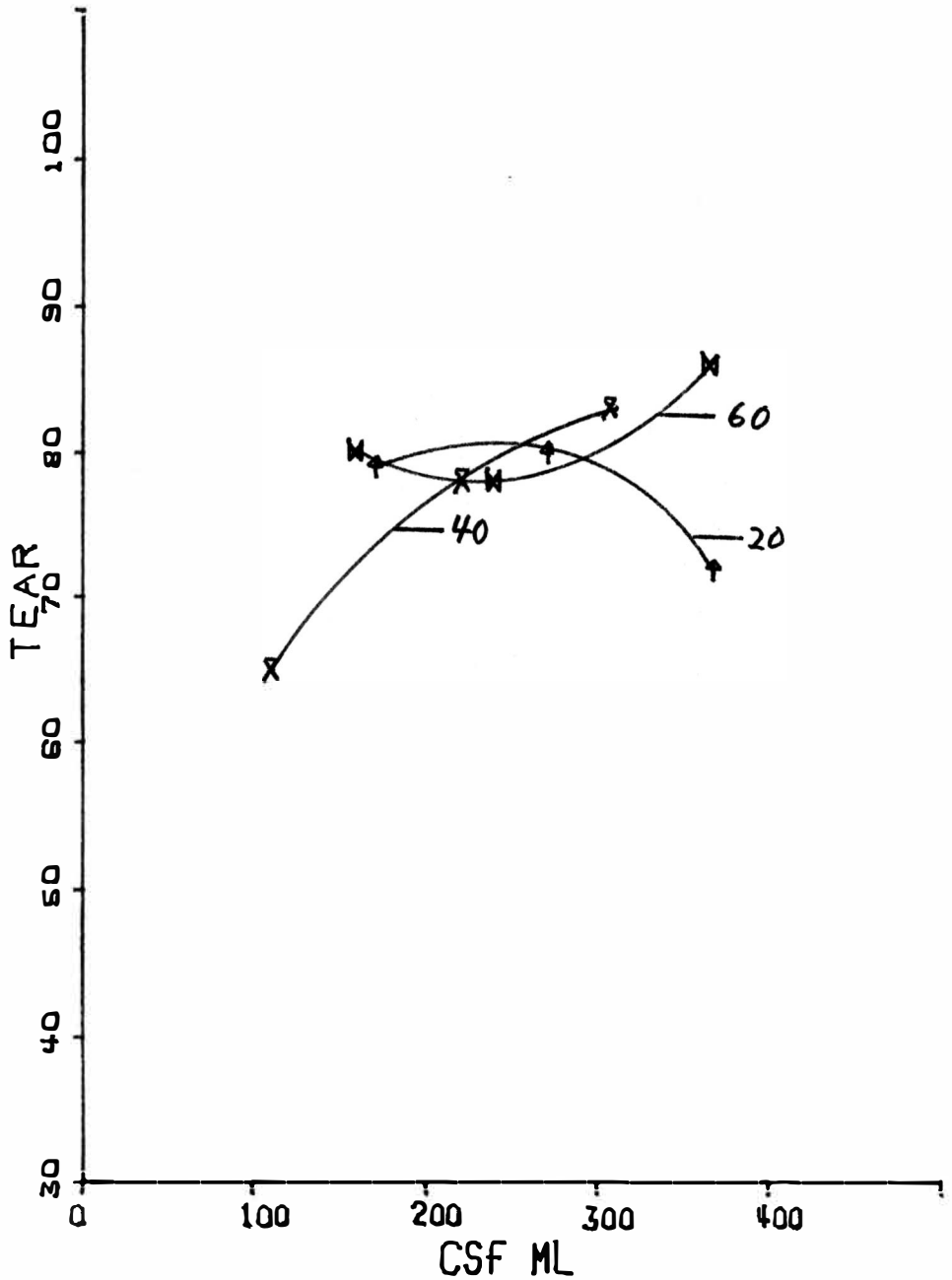
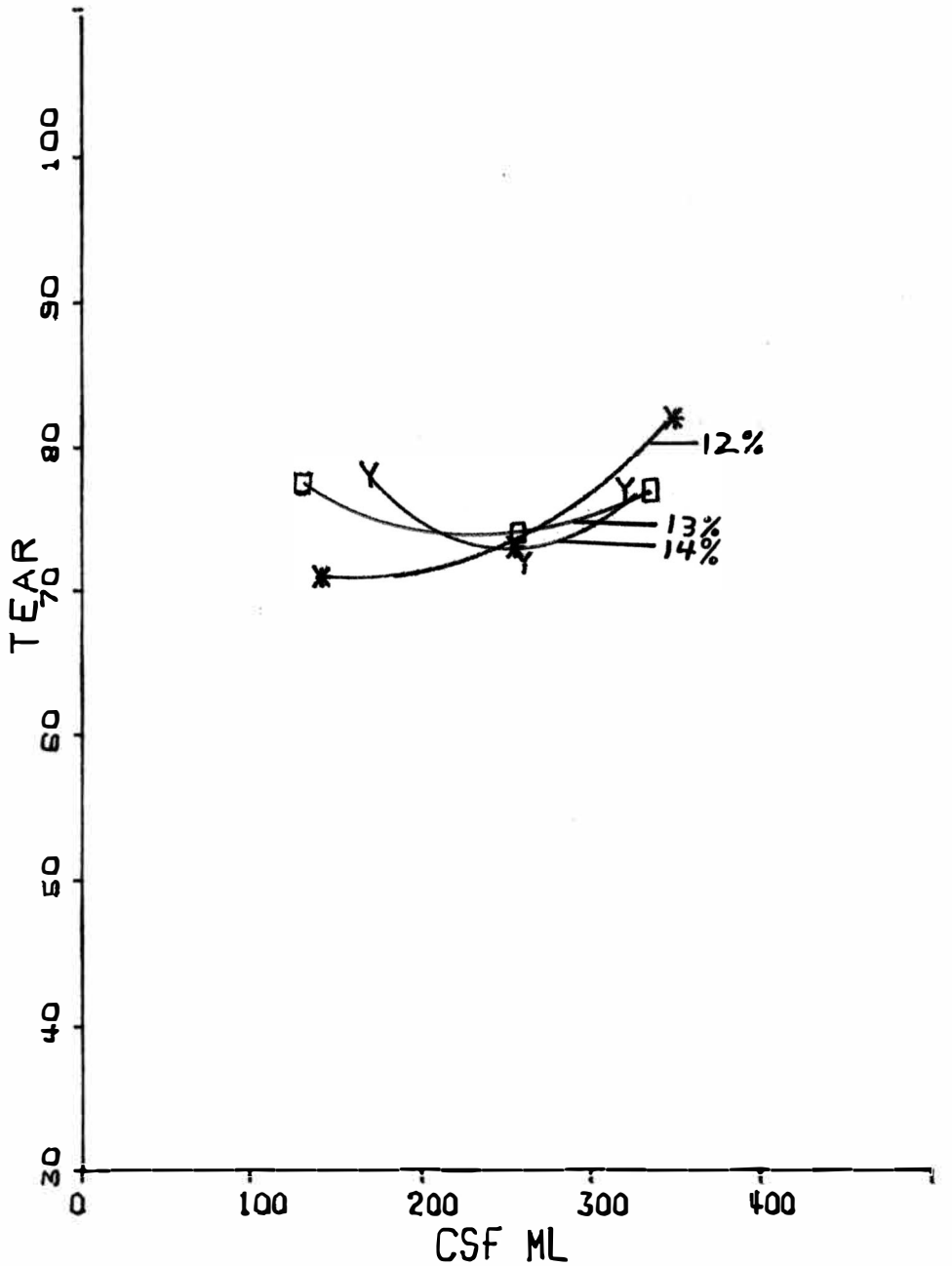
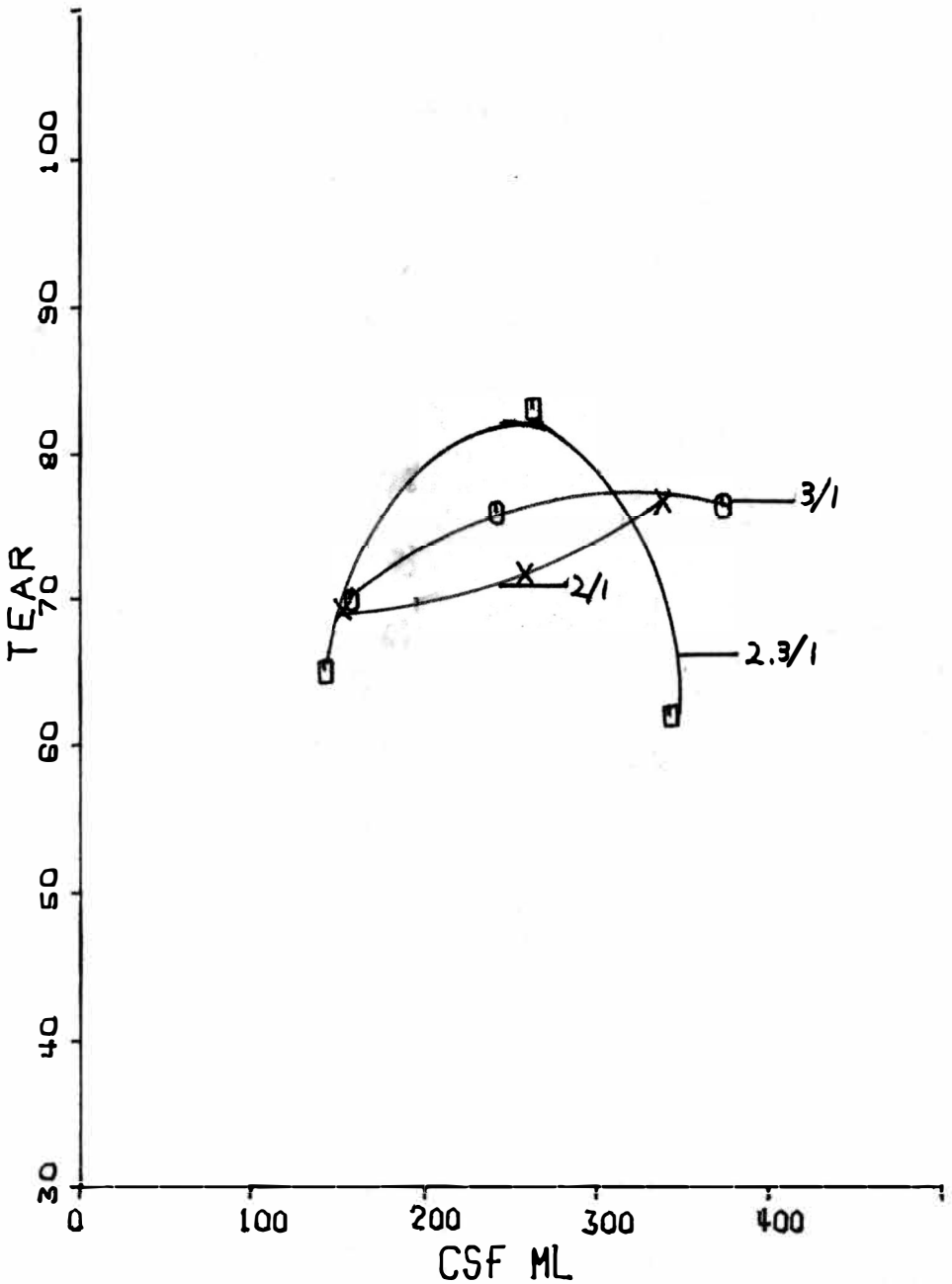


NSSC Controls-variable % chemicals



Variable ratio $Na_2CO_3/NaOH$



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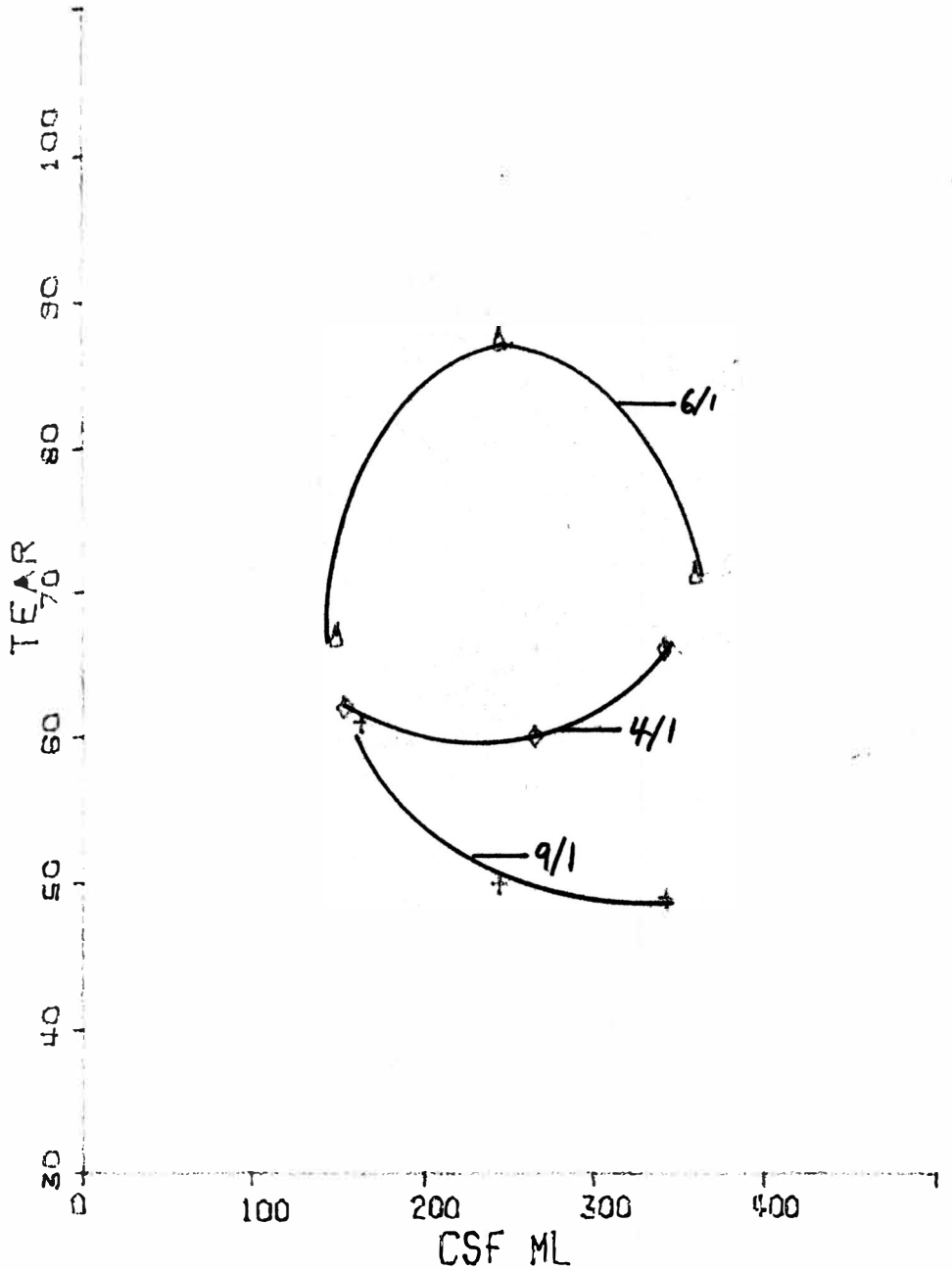
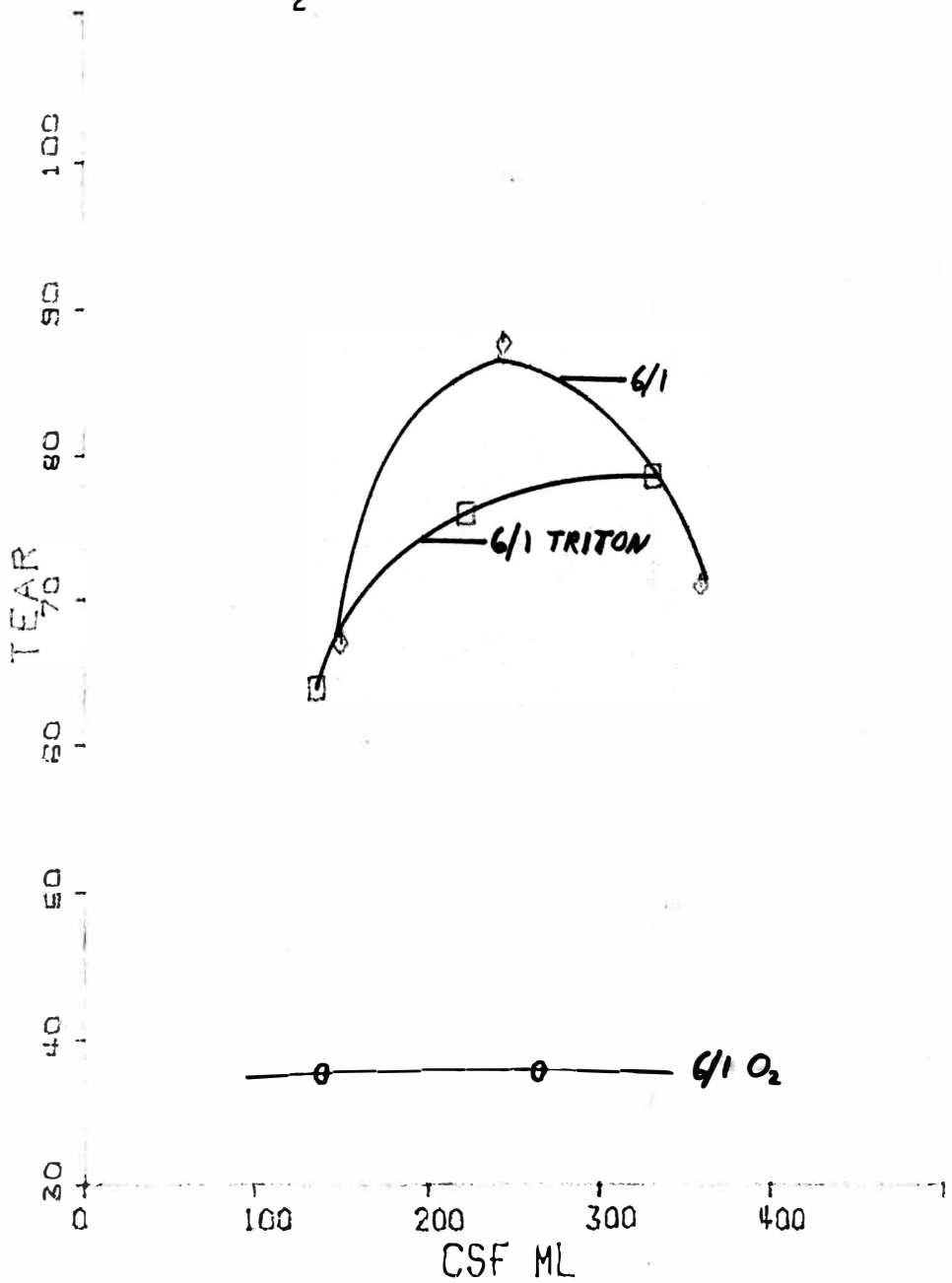


6/1,6/1 O_2, 6/1 Triton X-400



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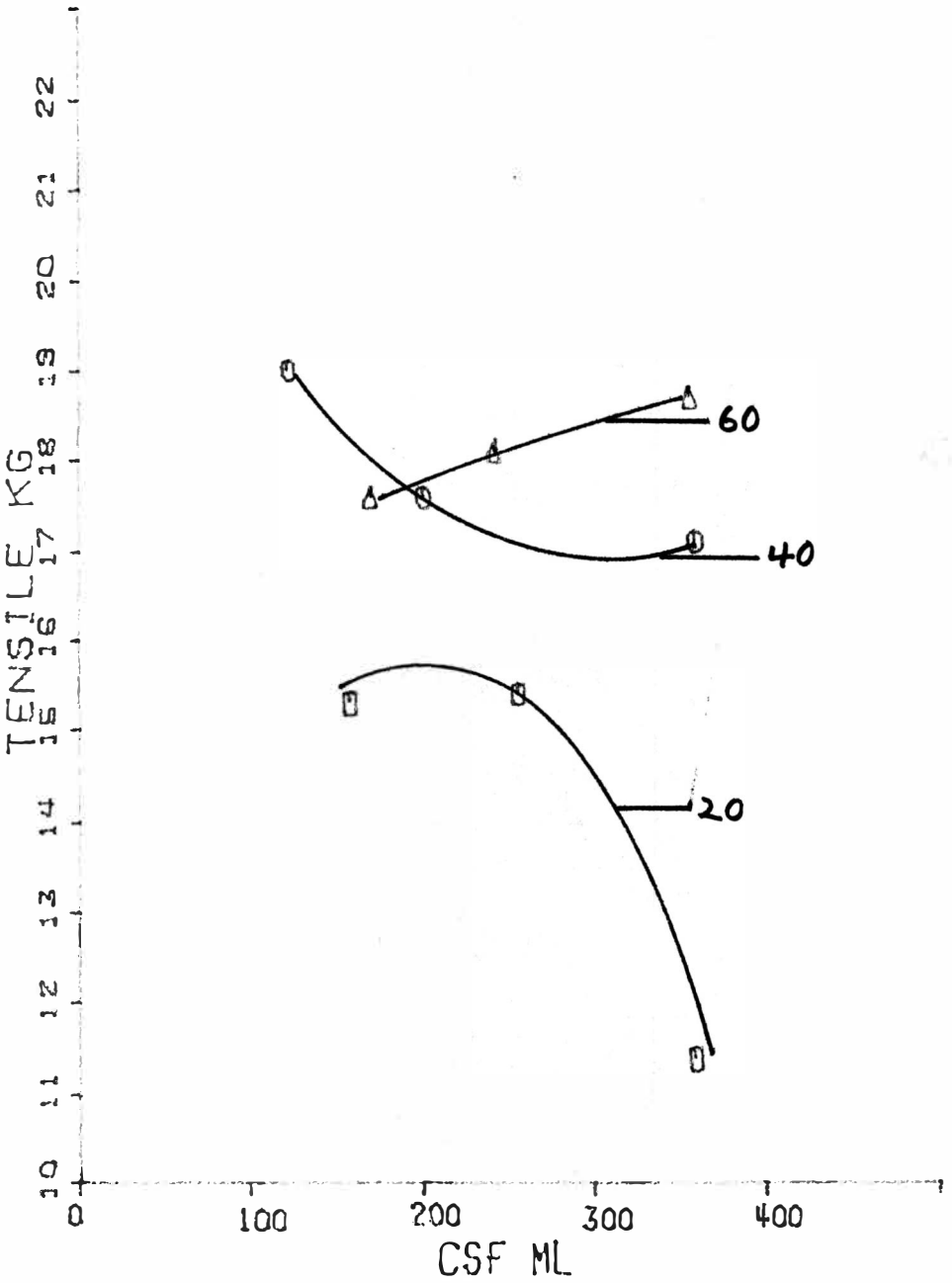

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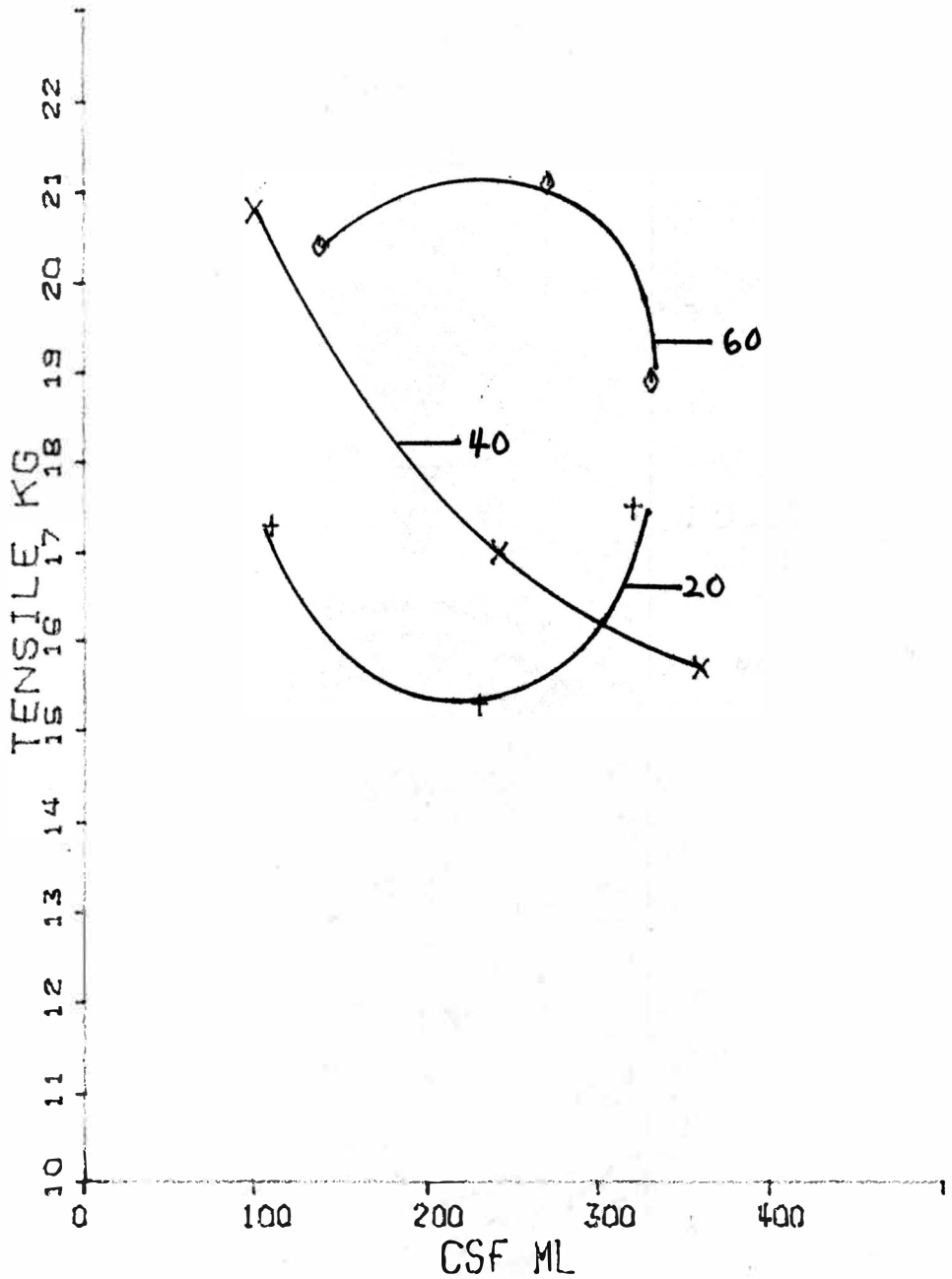

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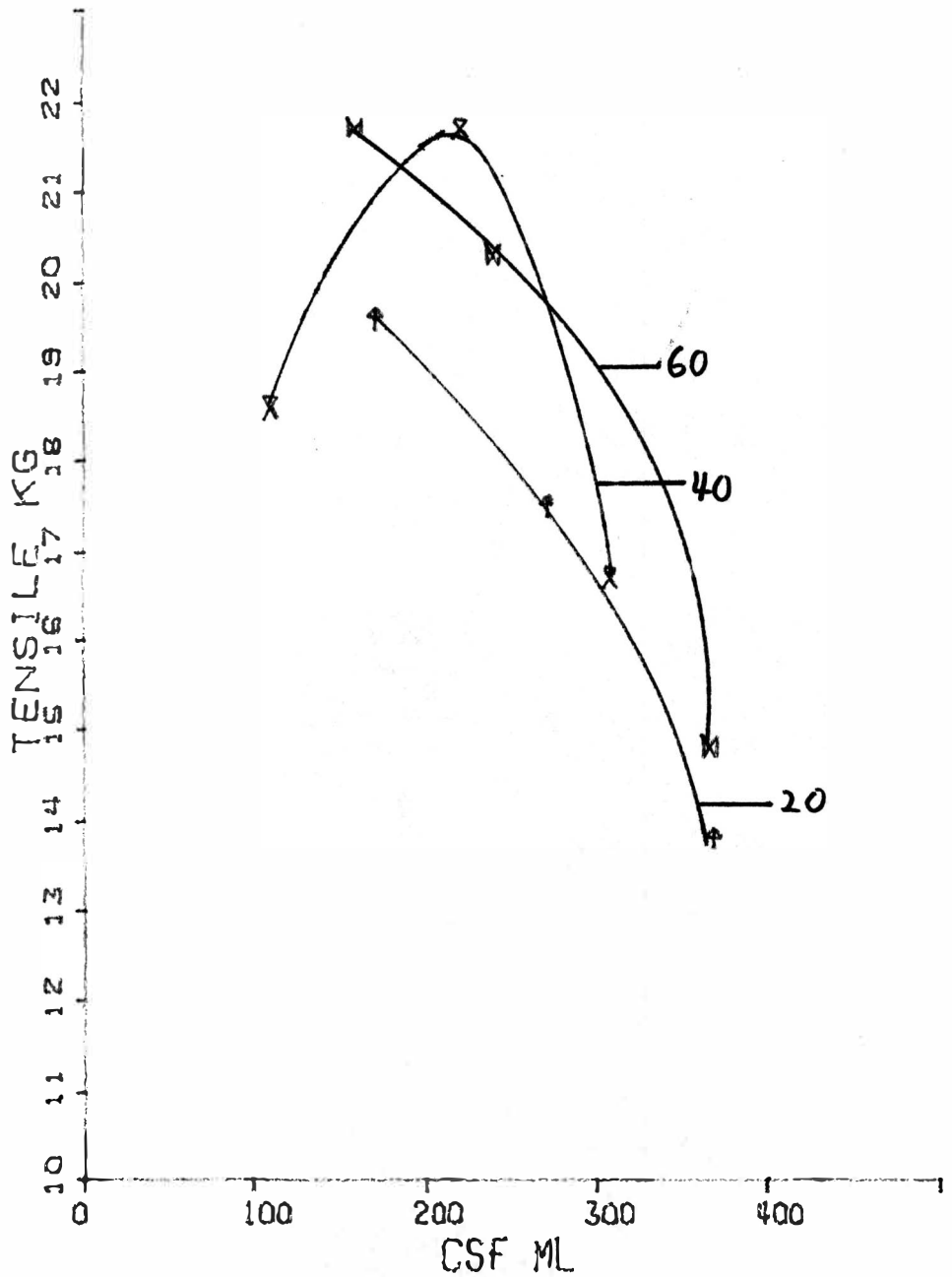
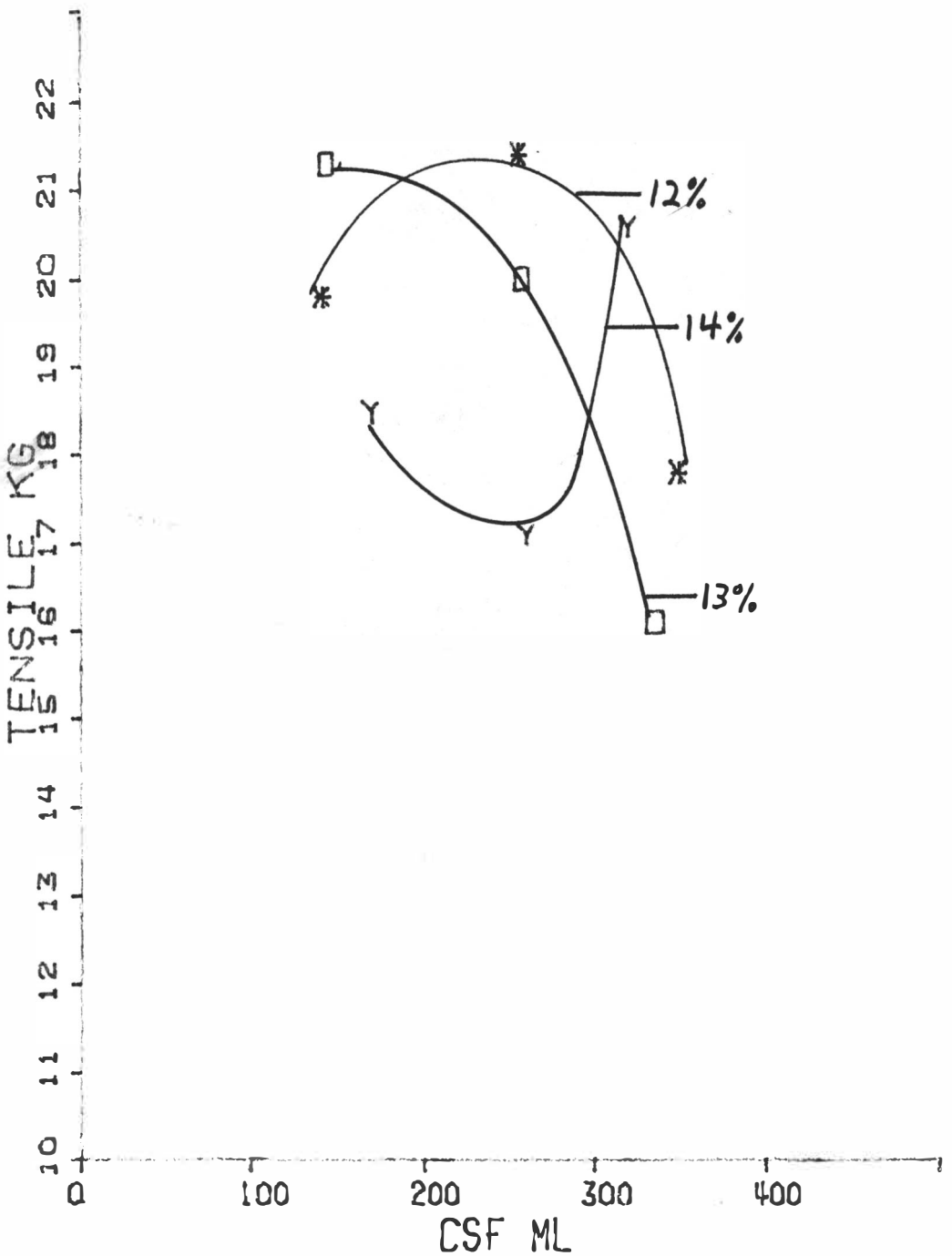


NSSC Controls variable chemicals



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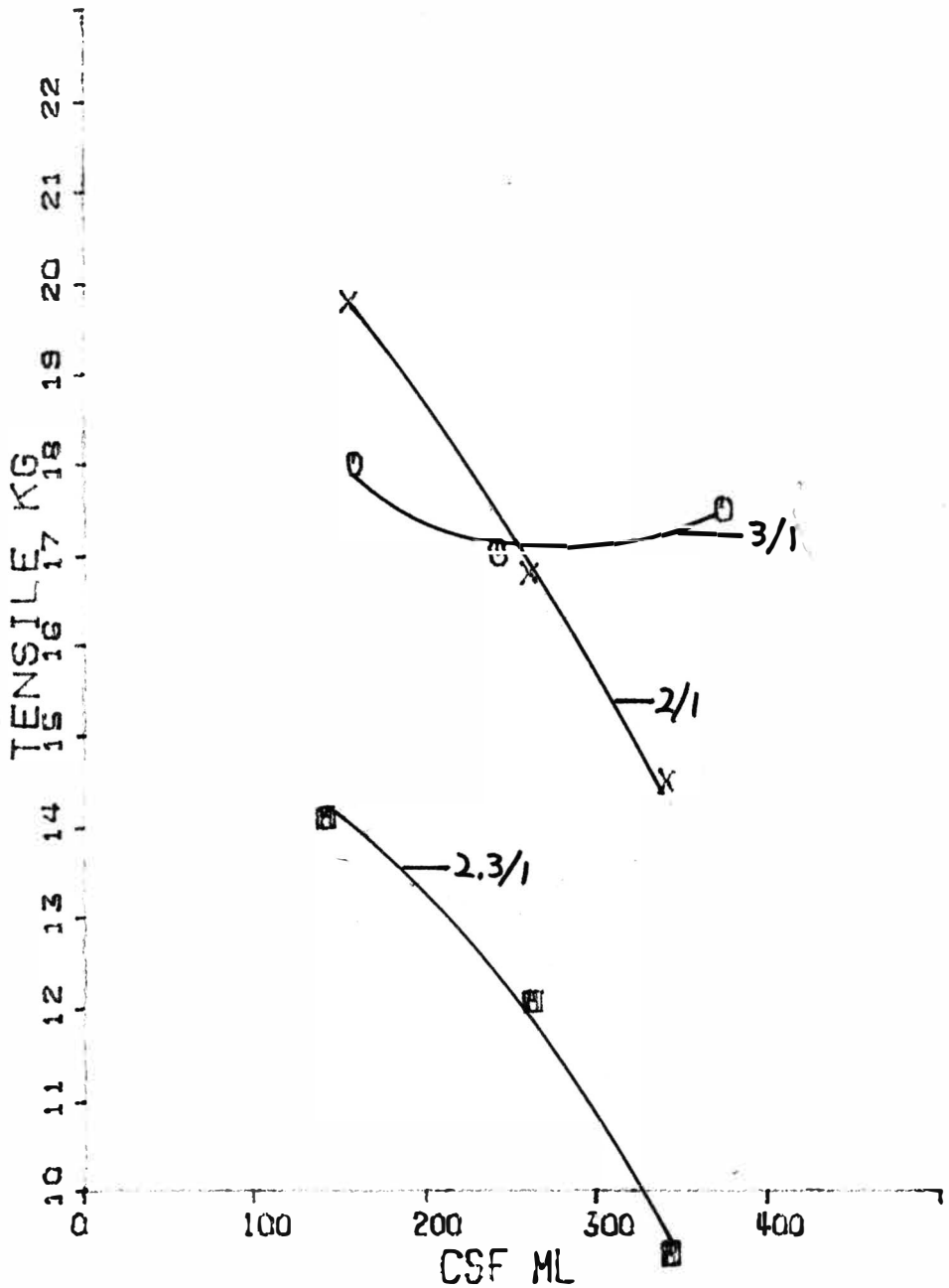
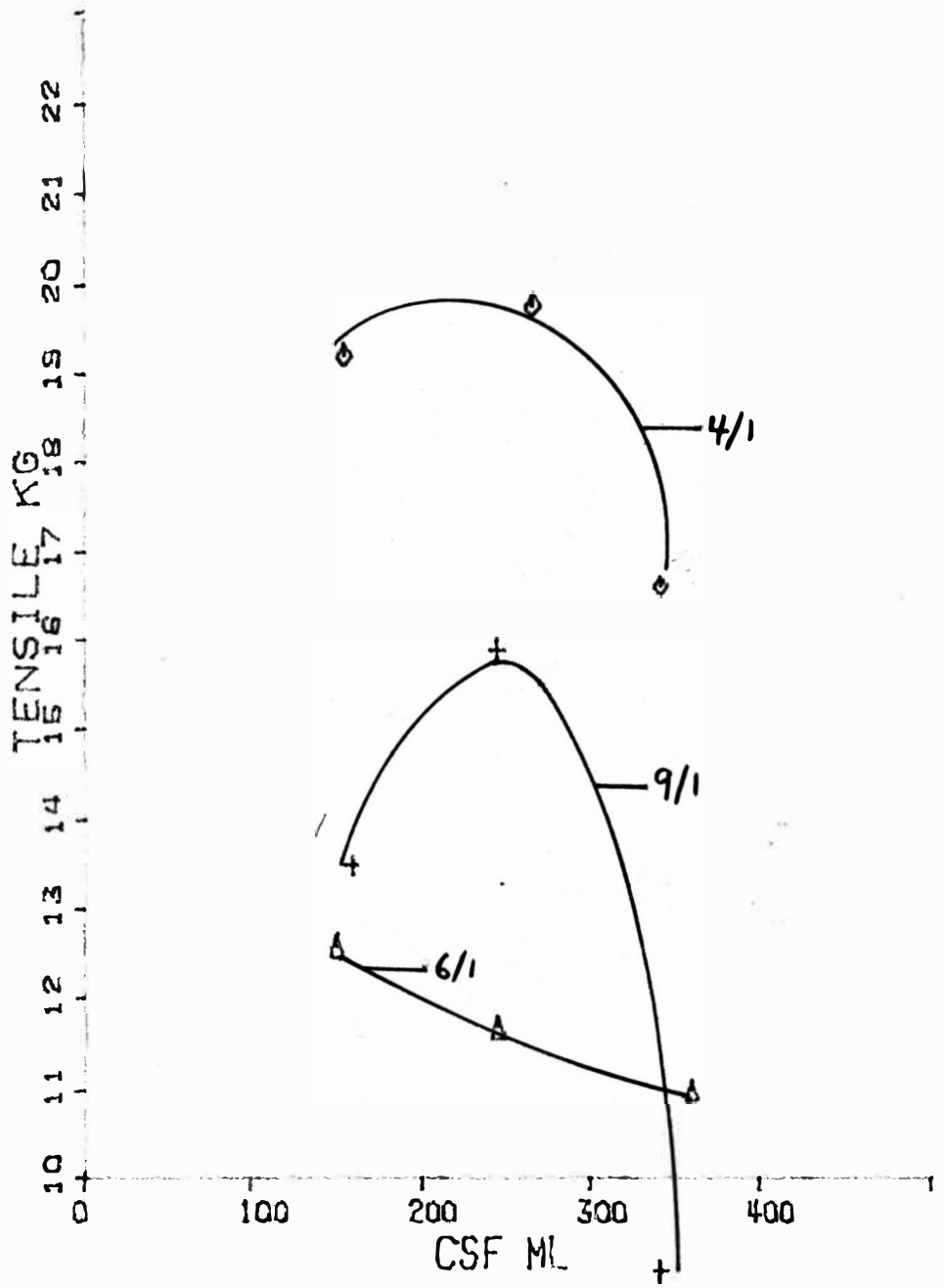
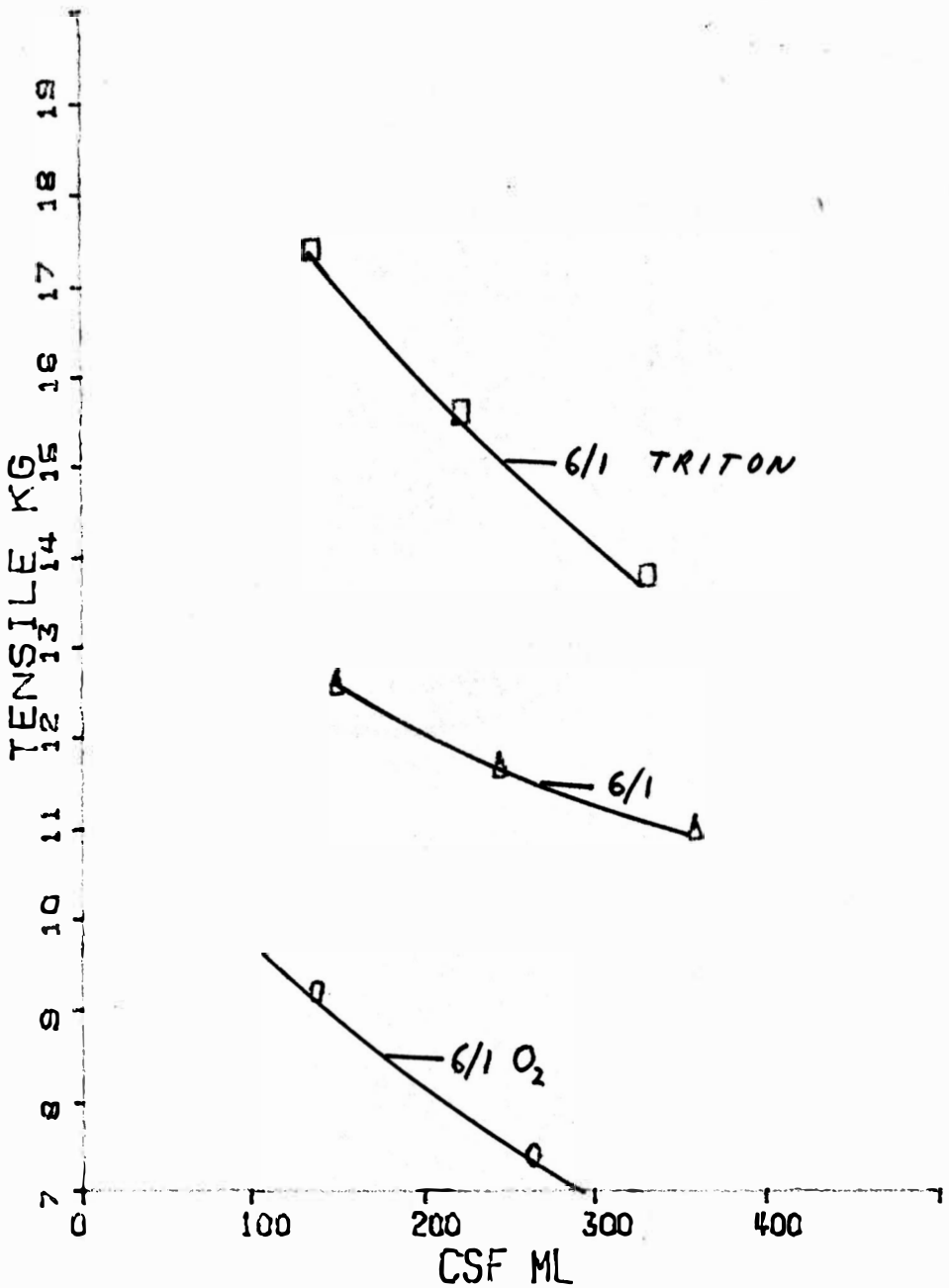


Variable ratio $Na_2CO_3/NaOH$



6/1, 6/1 O_2, 6/1 Triton X-400



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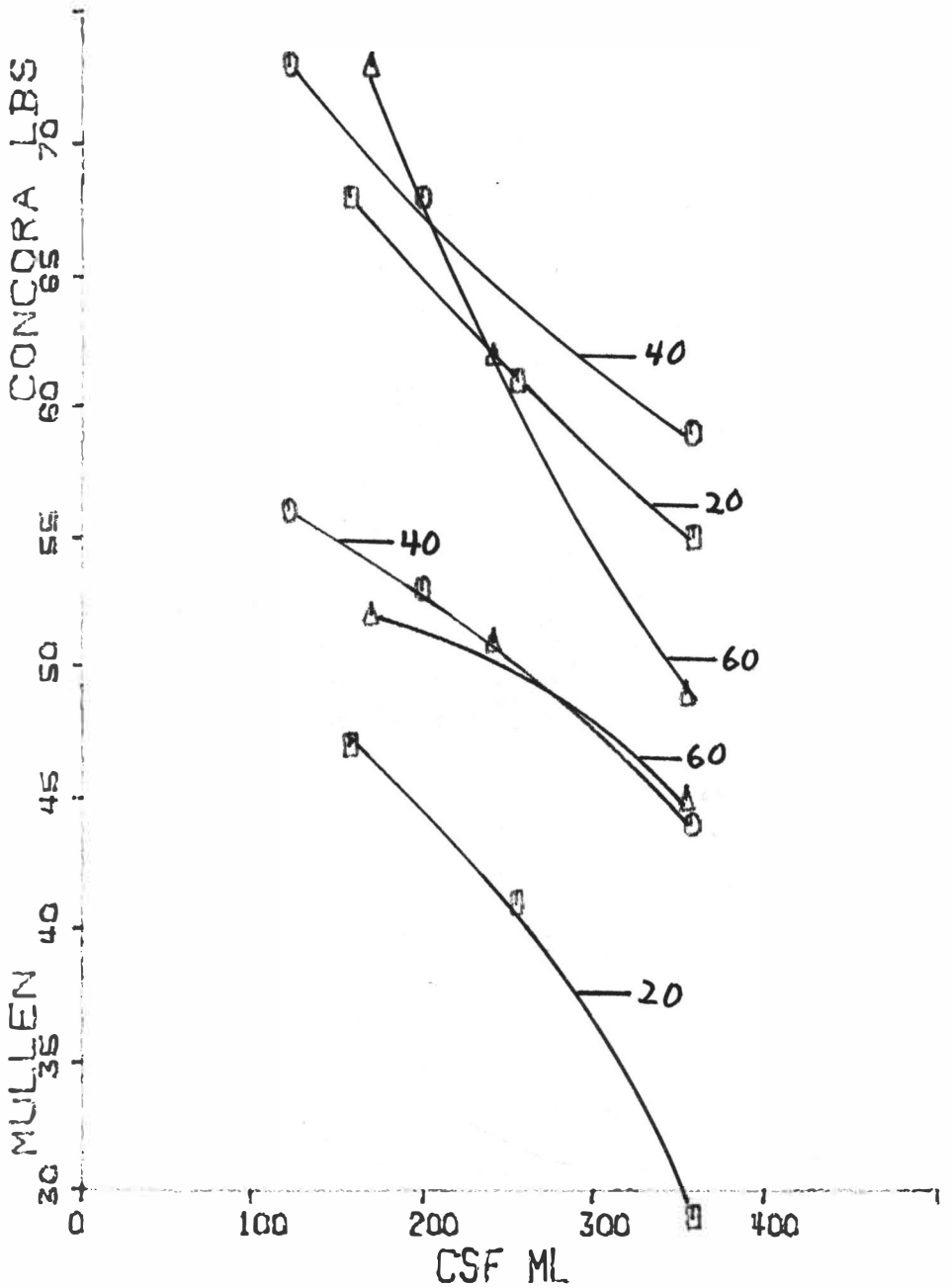

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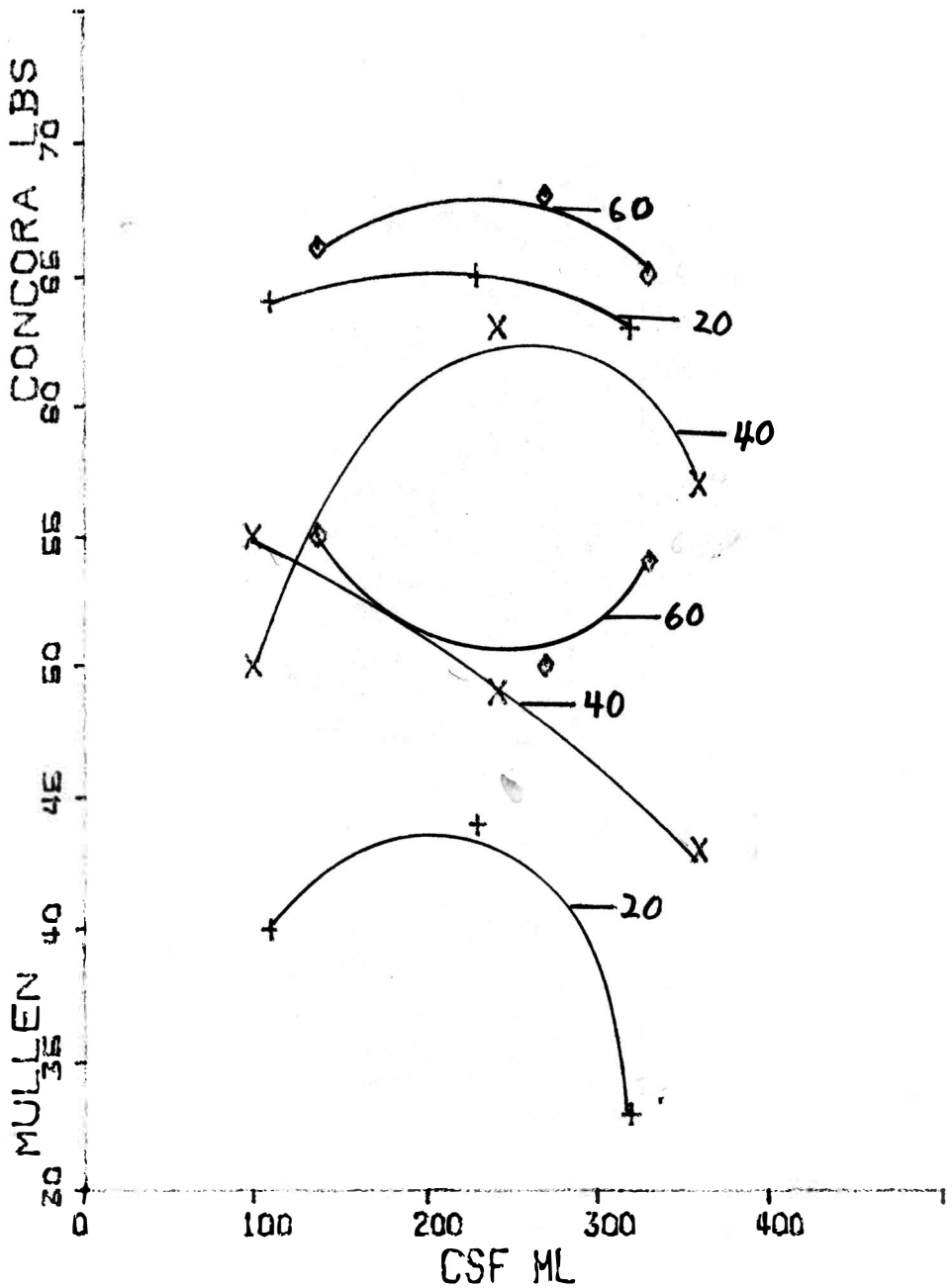

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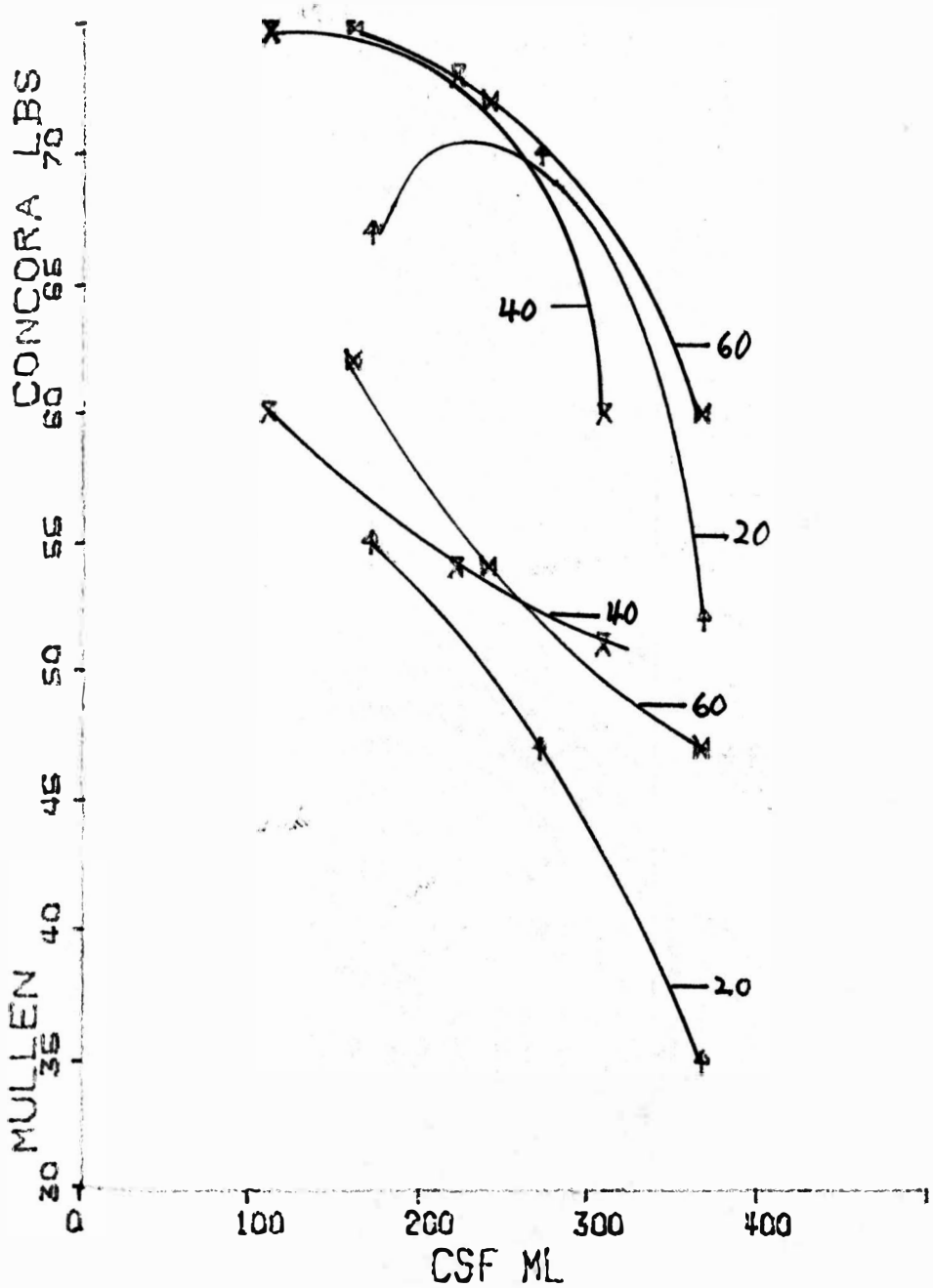

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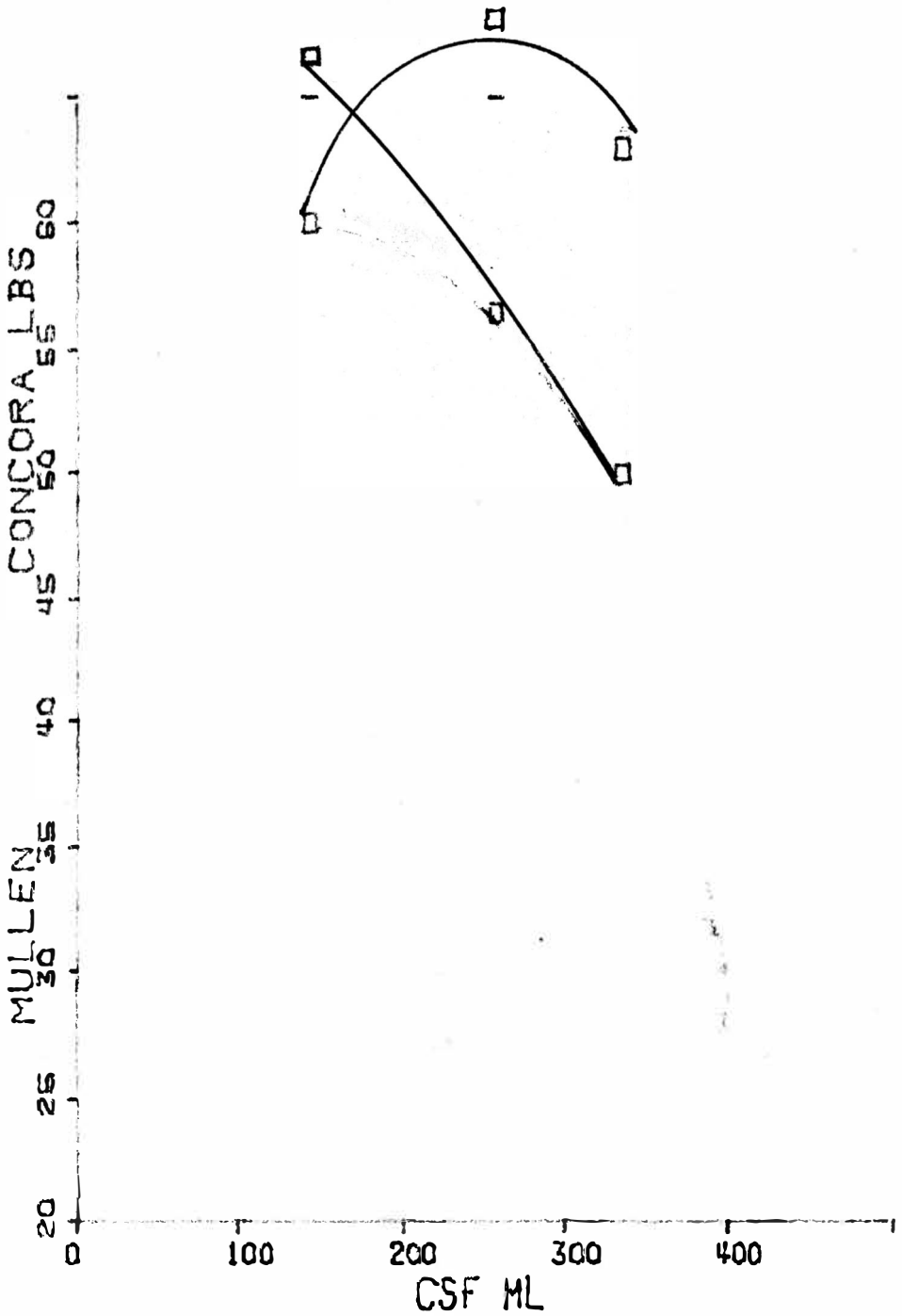
CONCORA LBS
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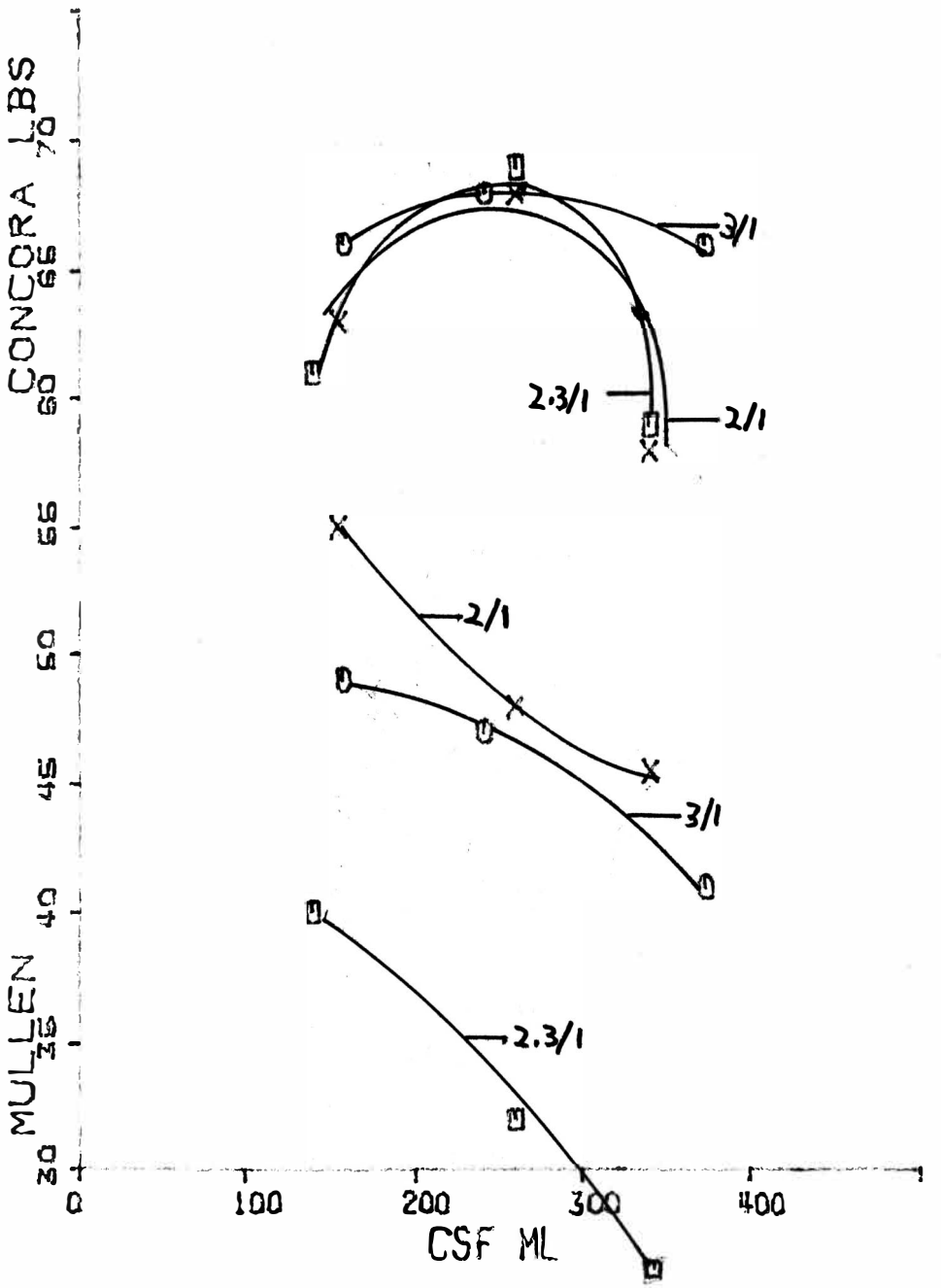
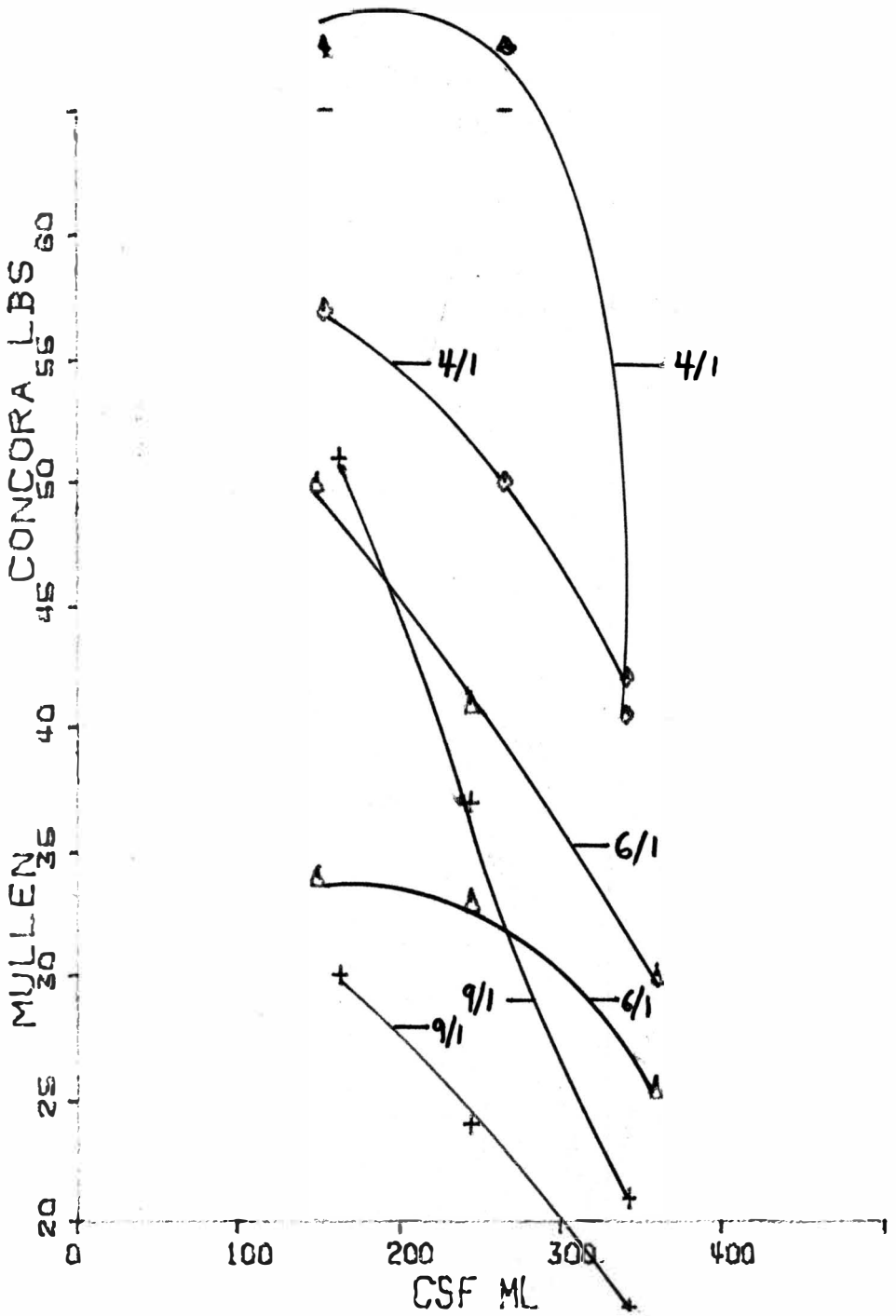
CSF ML

Variable ratio $Na_2CO_3/NaOH$



Variable ratio $Na_2CO_3/NaOH$



6/1, 6/1 O_2, 6/1 Triton X-400