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# A Study of Reuse and Possible Disposal of Clarified Cooking Liquors from Deinking Systems

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# A STUDY OF REUSE AND POSSIBLE DISPOSAL OF CLARIFIED COOKING LIQUORS FROM DEINKING SYSTEMS

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Contents

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Recovery or partial reuse of spent cooking liquors, originating in the manufacture of chemical and semi-chemical wood pulps, has been explored very thoroughly. The recovery or reuse of these spent cooking liquors has been of great economical significance to the paper industry.

Limited information has been available on the reuse of spent cooking liquors from deinking systems.

Bailey & Nadelman (1) conducted experiments with spent deinking liquor and investigated the possibility of reusing it. The authors found that, in terms of caustic soda, the actual alkali consumption during deinking was 0.24 - 0.90 percent based on the weight of paper as received. These quantities were less than one fourth of the alkali added for deinking. Therefore, the spent liquor contained at the end of the deinking cycle about three fourths of the alkali present at the start, plus soaps, clay and other dissolved and suspended materials. It was found, that the caustic percentage decreased with reuse, while the carbonate and possibly bicarbonate percentage increased proportionately. The total alkalinity remained nearly constant during repeated use of the liquor. The authors assumed that if the deinked stock was passed over vacuum filters, up to 85 percent of the

spent liquor could be recovered. Therefore, it was concluded that reusing deinking liquor is an economical operation. This assumption was confirmed by Goodwill (2). The same author (3) summarized the work done on alkali and heat recovery in deinking systems at a later date.

A search for information on dissolved solids in deinking liquors yielded the following results: Palladino (4) found that dissolved solids range from 1000 - 3500 ppm depending on type of washer used in production operations.From these solids 50 - 67 percent were volatile. Working on twelve deinking waste samples, Thompson, Swanson and Sears (5) found that, After settling, there were 34.0 to 44.8 pounds per 1000 gallons of soluble solids solids, equivalent to 4,098 to 5,400 ppm of dissolved solids.

Newton & Nadelman (7) reported thatin deinking mill effluent the concentration of dissolved and suspended solids was 3,720 ppm, of which the volatile portion was 46.0 percent and ash portion 54.0 percent. Further, the authors found that the concentration of suspended solids was 2,440 ppm, therefore indicating that the concentration of dissolved solids was 1,280 ppm.

The literature survey has shown that there has been no attempt made in studying the relationship between

dissolved solids content of spent deinking liquor and its suitability for reuse. Therefore, it has been planned to find out to what solids content clarified cooking liquor can be built up by reuse and repeated adding of the necessary make-up chemicals. Furthermore, it has been intended to determine some chemical and physical characteristics of dissolved solids, obtained from repeatedly used deinking liquor.

## Literature Cited


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6. Morgan, P.F., Tech. Bull. no. 5, National Council for Stream Improvement, New York, N.Y. (August 1946)
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## Experimental Design

OBJECTIVE: It is intended to find out to what solids content clarified deinking cooking liquor can be built up by reuse and repeated adding of necessary make-up chemicals. The dissolved solids will be analyzed for physical and chemical characteristics.

EQUIPMENT TO BE USED: Paper cutter, Morden slushmaker, large and small pails, titration equipment (burettes, pipettes, 125 ml flasks), calorimeter, analytical and triple-beam balances, fruit press, glass and metal beakers and other containers.

EXPERIMENTAL DETAILS: In order to find out to what solids content clarified deinking liquor can be built by reuse and repeated adding of the necessary make-up chemicals, the following experimental design is proposed:

Life magazine, after removal of covers, is to be cut to small squares about $\frac{1}{2} \times \frac{1}{2}$ inches in size. This paper is to be agitated for one half hour at 170 F at five percent consistency in presence of four percent caustic soda based on weight of paper on weight of paper without correction for moisture. After the cooking cycle, the deinked stock is to be filtered. The filter cakes are to be dewatered further by means of a fruit press.

The resulting cooking liquor is to be clarified either by sedimentation, filtration or treatment in a high speed

centrifuge. Part of the clarified deinking liquor is to be analyzed for total dissolved solids, ash of dissolved solids, alkali content, pH value and specific gravity.

The balance of the deinking liquor is to be reinforced by addition of one percent caustic soda based on the weight of waste paper to be used, and is to be reused repeatedly. At the start, 30 lb of cut paper is to be employed. The reuse of recovered spent cooking liquor is to be limited to nine cycles. Thus, ten samples of cooking liquor will be obtained for analysis and evaluation.

## Experimental Procedure

In order to put the experimental design into effect, the following methods were employed:

Life magazine, after removal of covers, was torn to approximately 1 × 1 in. pieces.

It was decided to start with 30.0 lb of magazine paper for the first experiment, and to decrease the amount in half for each succeeding step ( experiments two through ten ).

In experiments one, two and three, each full size batch, treated in the Slushmaker consisted of 1,500 grams of paper as received, four percent of caustic soda based on the weight of the paper and enough hot water to yield about five percent consistency at the end of the deinking cycle. The mixture was agitated for 30 minutes at 170 F. This temperature was reached and maintained by introducing direct steam. Proper allowance was made for the condensate formed by the steam. Experience showed that about 4.5 lb of water was introduced by condensation of the steam for each full size batch.

After deinking, the contents of the Slushmaker was emptied into a crock and 30 ml of 35 percent formaldehyde solution added as preservative. After cooling, most of the liquor was separated from the fibers with the help of a fruit press. The filter cakes were discarded. Part of the recovered liquor was fortified by adding one percent caustic soda based on the weight of the fresh paper sample. The fortified liquor was used for the next experiment. A total of ten deinking ex-

periments were carried out. Samples of each liquor were set aside for analyses.

As stated, the volume of the deinking mixture for each experiment decreased with each reuse of liquor. After the sixth experiment, the volume was not sufficiently large for agitation in the Slushmaker. Deinking experiments six through eight were carried out using a metal pail and a large agitator. Temperature of the mixture was raised by pre-heating and maintained at constant level with the help of a hot plate. The last two magazine samples ( experiments nine and ten ) were deinked in large metal beakers using a small electric stirrer.

All samples of cooking liquor, intended for analysis, were placed in glass jars and graduated cylinders and were allowed to stand for about 20 days. It was hoped, that the suspended particles would settle by gravity during this period and a clear liquid would remain for analysis. The experimental work showed, that the settling rate of the suspended solids decreased with increase in frequency of reuse. Filtering of the liquor samples was extremely slow, due to clogging of filter paper.

For analysis, the clarified portions from top of each container were taken and filtered to remove any suspended particles. In this manner enough liquor from each sample was collected to make analysis of the liquor free from suspended solids possible.

The following tests were performed on each liquor sample:

a) pH

b) specific gravity at 20 C

c) total dissolved solids

d) ash of dissolved solids

e) total alkalinity

The pH of the liquor samples was determined by means of a Beckman pH meter.

The specific gravity was determined at 20 C using a pycnometer bottle. First, the water value was obtained as the difference in weight between the empty pycnometer bottle and the same when filled with distilled water at 20 C. Then the liquor value was determined by taking the difference in weight of the empty pycnometer bottle, and when filled with clarified cooking liquor. Specific gravity of a liquor sample was calculated by dividing its liquor value by the water value.

The total dissolved solids were obtained by evaporating the clarified liquor sample of known volume and by determining the weight of the solids left. The results were expressed in percent solids as well as in parts per million.

The residue left after the dry dissolved solids sample had been heated at 800 C in a muffle furnace, was the ash of dissolved solids and expressed in percent of the total dissolved solids.

Total alkalinity determination was carried out only for the the samples of the first seven experiments. It was observed, that the pH values of all samples had dropped to the extent of one to two units, because of failing effect of the preservative. For samples, still possessing a pH of above 8, the alkalinity

value was determined by titrating the liquor with 0.115 N HCl and by using a zeromatic pH meter for end point observation.

## Presentation and Discussion of Results

### Specific Gravity:

The experiment shows that the specific gravity of the cooking liquors increases with repeated use. After the first experiment the specific gravity was 1.0024, and after the tenth experiment it reached the value of 1.0157. The latter is about equivalent to a two percent sodium carbonate or a four percent starch solution. As was found experimentally, the maximum total dissolved solids in the liquor amounted to 2.8 percent. The increasing specific gravity indicated a building up of dissolved solids with repeated use. After the sixth use, the value of specific gravity experienced a rapid rise following each additional reuse (Table I and Fig. 1).

### Total Dissolved Solids Content:

From the experimental results it can be seen that the total dissolved solids content increased after each reuse of the liquor. After the first experiment, the liquor contained 8,944 ppm of dissolved solids. This value increased, slowly at first, and after six experiments rapidly to a final value of 28,286 ppm. The dissolved solids consisted of both organic and mineral matter (Table II and Fig. 1).

### Percent Ash of Dissolved Solids:

The percent of ash represents the mineral fraction of the dissolved solids. After the first experiment, the cooking liquor contained 8,944 ppm of dissolved solids with 2,660 ppm or 29.7 percent of these being of mineral nature. With conti-

## SUMMARY OF DATA

### Table I. Specific Gravity at 20 C

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 1.0024 | 1.0035 | 1.0054 | 1.0059 | 1.0060 | 1.0063 | 1.0076 | 1.0094 | 1.0120 | 1.0157 |

### Table II. Total Dissolved Solids, ppm

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 8,944 | 11,867 | 12,718 | 13,388 | 13,970 | 14,126 | 18,512 | 19,666 | 21,638 | 28,286 |

### Table III. Ash of Dissolved Solids, percent

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 29.7 | 28.7 | 40.0 | 23.2 | 20.3 | 34.0 | 19.1 | 19.6 | 19.8 | 19.2 |

### Ash of Dissolved Solids, ppm

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2,660 | 3,420 | 5,080 | 3,100 | 2,840 | 4,800 | 3,540 | 3,860 | 4,260 | 5.400 |

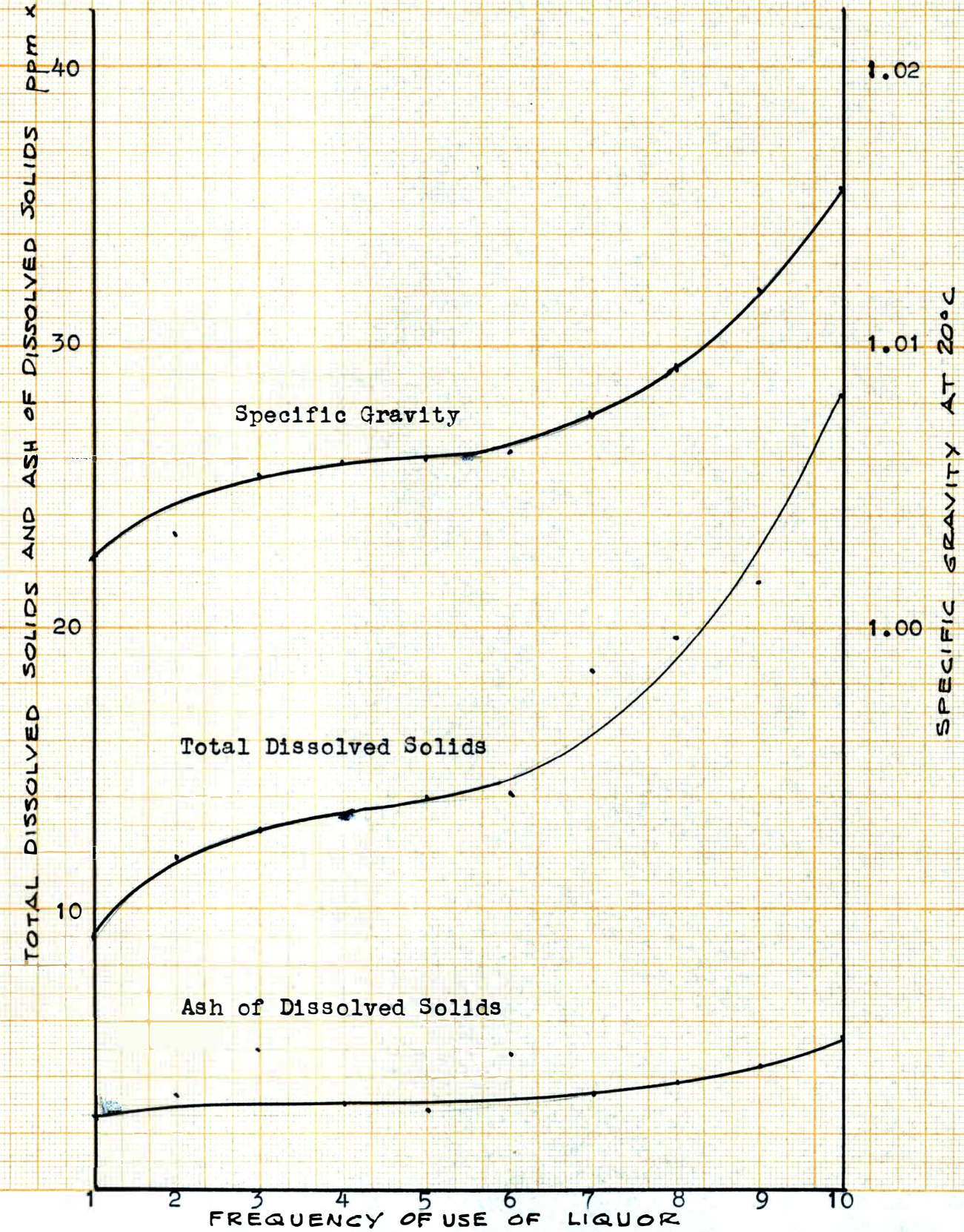
### Table IV. pH Value

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 9.80 | 9.47 | 9.33 | 9.35 | 9.38 | 9.50 | 9.40 | 9.10 | 9.39 | 9.40 |

### pH Value after three weeks standing

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 8.2 | 8.5 | 8.4 | 8.4 | 8.1 | 6.8 | 8.4 | 7.4 | 7.5 | 7.3 |

Graph 1.
EFFECT ON PROPERTIES OF COOKING LIQUOR CAUSED BY REPEATED USE.



nuous reuse the dissolved inorganic solids experienced only a very slight build-up, indicating that the rapid increase in total dissolved solids was largely due to dissolved organic matter. The dissolved solids increased by 19,342 ppm, this being the difference in dissolved solids contents after the first and the tenth experiment. In comparison, the ash value of dissolved solids increased only by 2,740 ppm during the same time (Table III and Fig. 1).

pH value:

The pH value for all cooking liquor samples remained nearly constant, between 9.3 and 9.5. It was observed that after three weeks standing the pH values dropped several units due to the failing strength of the preservative (Table IV). The high value for liquor sample number seven after three weeks standing was caused by the use of a relatively large quantity of the preservative.

Figure 1 shows graphically the build-up of specific gravity, total dissolved solids and ash of dissolved solids throughout ten deinking experiments when clarified and fortified cooking liquor was reused.

## Conclusions

From the above results the following conclusions may be drawn:

a) Reuse of clarified cooking liquor, after fortification, was studied and proven feasible through at least ten cycles.

b) Dissolved solids content of the reused and regularly fortified liquor after ten deinking cycles was about 2.8 percent as compared to 0.9 percent after first deinking experiment.

c) The 2.8 percent of dissolved solids found in the liquor after the tenth deinking cycle consisted of

0.53 percent mineral matter in form of ash

0.27 percent volatile matter mostly organic in nature

d) Stock deinked with the several times reused liquor was at least equal in quality to stock deinked with a freshly prepared caustic soda solution.

e) The cost of clarifying, evaporating and burning the reused deinking liquor with only 2.8 percent solids content on a commercial scale would be prohibitive.

## Summary

Ten deinking experiments were carried out and the liquor samples removed were subjected to analysis for chemical and physical properties. These analyses lead to the following conclusions:

a) Clarified cooking liquor, with regular fortification, may be reused for at least ten cycles.

b) Dissolved solids content of the liquor increases from 0.9 percent after one deinking cycle to 2.8 percent after ten deinking cycles.

c) The 2.8 percent of dissolved solids found in the liquor after the tenth deinking cycle consisted of 19.2 percent ash.

d) Stock deinked with the several times reused liquor was at least equal in quality to stock deinked with a freshly prepared caustic soda solution.

e) The cost of clarifying, evaporating and burning the reused deinking liquor with only 2.8 percent solids content on a commercial scale would be prohibitive.