Characteristics of combined effluent treatment sludges from several types of pulp and paper mills

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Combined sludges from 7 primary–secondary effluent treatment systems serving 10 highly diversified pulp and paper operations on the Upper Wisconsin River were analyzed for total solids, carbohydrates, ash, and elemental composition, including plant nutrients and heavy metals. The characteristics of the 7 sludges varied several-fold with pulping and papermaking processes and operations and effluent treatment. Balances were developed between wood and process chemical elements and those elements of the sludges. The suitability of the sludges for land spreading and incineration is considered.

Keywords: Sludge • Combustion • Chemical composition • Land use

A group of 10 pulp and paper mills, mostly wood-based, located on a 50-mile stretch of the Upper Wisconsin River, progressed in effluent treatment from earlier paper mill save-alls to primary effluent clarifiers in the early 1970's and finally to full treatment with secondary effluent treatment using activated sludge systems by 1977. The pulp and paper operations, served by 7 treatment systems, covered a wide range of pulping processes and paper products, as shown in Table I.

The objectives of our study were: (a) to determine the production rates and characteristics of the combined primary and secondary sludges from the 7 treatment systems, (b) to relate these sludge production rates and characteristics of the wood, process, and treatment parameters, and (c) to consider the utilization of the sludges with respect to their characteristics. The combined primary and secondary sludges are presently being sent to landfills.

Discussion

Classification of pulp and paper operations

We studied 7 primary–secondary effluent treatment plants serving 7 integrated wood pulp mills, an integrated recycling mill, a nonintegrated paper mill with a recycling paperboard operation, and a kraft-wood pulp mill. Two of the treatment plants were operated centrally for two or more individual pulp and paper operations.

Process/ grade	*Operation/ mill no.*	*Daily capacity (1), a.d. tons*
	Pulp	
Kraft	3	999
Sulfite	3	631
Mechanical	2	544
Recycled	2	153
	10	2327[a]
	Paper	
Fine/business	5	1679
Coatedbook	3	1622
Other	2	343
Total	10	3644

[a] Bleached, 1490 tons; brightened, 544 tons; unbleached,293tone

1. **Pulping processes, paper grades, and daily mill capacities**

The pulping processes included kraft, sulfite (calcium and magnesium base), stone groundwood, thermomechanical, and recycling (Table I). Eighty-five percent of the chemical and deinked pulps were bleached, and all the mechanical pulp was brightened (Table I). The chemical pulp mills had rated daily capacities of 200–400 a.d. tons, and the mechanical type were of 200-ton capacity. The paper grades ranged from fine/business to coated groundwood printing to unbleached kraft specialty, with a small production of paperboard. The paper mills had daily capacities of 250–530 tons, except for the small-production paperboard and deinking paper mills. The integrated pulp mills supplied about 60% of the fiber for papermaking, the difference being made up by purchased pulp.

Sludge production and gross characteristics

The total daily production of combined sludges from the 7 treatment plants in early 1980 was 221 a.d. tons (199

II. Production and gross characteristics of sludges

	Avg.	Range
Production,[a] tons/ton[b]	0.04	0.02-0.09
Total solids, %	21	17.8-28.5
Total carbo-hydrates, %	30.3	23.5-36.2
Ash, %	33.5	27.7-38.1
pH	...	6.8-7.3

[a]Total daily production for seven treatment plants = 221 dry tons (199 metric tons). [b]Units are tons of sludge/ton of pulp + paper, dry basis.

metric tons)(Table II). This amounts to 0.04 ton/ton of pulp + paper production from the associated mills. The sludge production from the individual mills varied widely from 0.02 to 0.09 ton/ton. This rate depends on (a) paper mill operation (grade changes, shutdowns, white water recycling, etc.), (b) proportion of purchased pulps, (c) chemical vs. mechanical pulp, (d) proportion of short hardwood and long softwood fibers, (e) pulp bleaching, (f) repulping and deinking, and other factors. The lowest rate, for example, was observed in a mill making mechanical pulp and using 55% purchased fiber. The highest rates were found in a recycling mill and a mill with an exceptionally high proportion of secondary sludge in its combined sludge product.

The total solids contents of the sludges from the 1980 sampling of the wood pulp mills varied from 17.8% to 28.5% (Table 11). The weighted average of all the sludges was 21%. The solids contents of sludges depends on (a) the proportion of primary sludge in the combined product, (b) the type of dewatering device, (c) the addition of filtering aids, (d) the operation of the treatment plant (for example, control of filamentous sludge), and other factors.

The results of the chemical analysis for total carbohydrate, ash, and pH are shown in Table II. The total carbohydrate value is an indicator of the relative fiber content of the sludges. The total carbohydrate value ranges from 23.5% to 36.2% for the wood pulp mills; the average was 30%. The magnitude of these results appears to depend on the process characteristics and fiber losses of the individual mills rather than on the general type of pulp mill. Similar data obtained in 1976 gave an average of 38% total carbohydrate, and this may indicate a general decrease in fiber losses from the mills since 1976. A deinking mill sludge would be expected to have a higher value than sludge from wood pulp mills because there is more unusable fiber generated when paper stock is recycled. The composition of the total carbohydrates was quite constant between the sludges of the various mills, and the average composition was about 65% glucan, 10% mannan, and 25% xylan.

The ash content of the sludges ranged from 27.7% to 38.1% and averaged 33.5%. The ash content appeared to depend on the grade of paper and mineral and coating additives used in the mill.

The pH levels of the sludges were from 6.8 to 7.3. In cases in which lime was added for improved drainage or odor control, the pH was in the low alkaline range.

Elemental composition of sludges

The wood, fresh process water, and pulping (including recovery make-up), bleaching, and papermaking chemicals introduce certain elements into the pulp and paper system. Corrosion and wear as well as surfactants and polymers added to control scales and to aid dewatering all supplement the elemental input. These elements leave the system in the pulp and paper products, the effluents, air emissions, and solid wastes. Those in the effluents appear in the sludges and in the treated water from the effluent treatment. A certain quantity remains inert in the pulp and paper system as so-called ballast chemicals, the amount being accentuated by closing the system.

The averages and ranges of macro- and microelements and other elements in the 7 sludges are given in Table 111. The levels of the individual elements depend, as noted above, on the amounts entering and leaving the system. Several of the elements, including N, P, K, Ca, Mg, Fe, Na, and Al, are present in relatively large quantities-over 0.1% or 1,000 ppm. An intermediate element is S. These elements enter the system mostly with the wood and in the treatment of the effluent. The remainder of the elements are relatively few and appear to be derived from pulping and bleaching chemical impurities and equipment corrosion and erosion. The range of elements from mill to mill was wide, up to nearly 40-fold for Ca, calcium compounds

III. Elemental analysis of sludges[a]

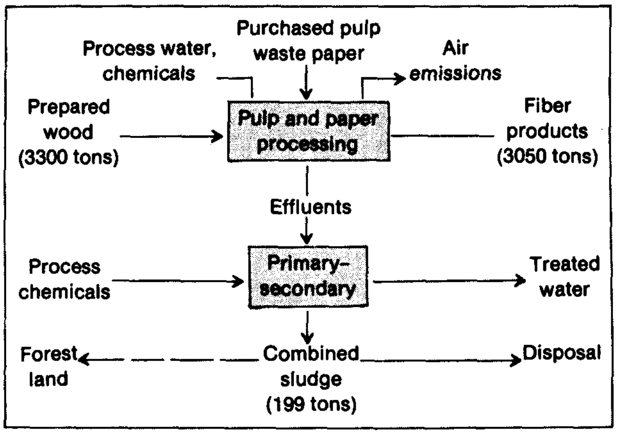
Element	*Avg.*	*Range*
Macro-elements,%		
N	2.9	0.14-4.1
P	0.34	0.125-0.58
K	0.137	0.037-0.595
Ca	2.95	0.266-9.02
Mg	0.065	0.011-0.100
Micro-elements,ppm		
Fe	2.930	675-7,162
B	13.3	8.5-21.1
Cu	67.4	2.2-90.9
Zn	127.0	41.3-213.6
Mn	119.0	22.9-286.4
Mo	6.7	5.2-8.9
Other elements, ppm		
Na	0.173[b]	0.049-0.412
Al	19,500	15,000-22,000
Cd	3.9	1.6-9.4
Cr	39.6	29.2-55.8
Pb	81.9	37.8-129.3
Hg	3.9	3.9

[a]Ovendry basis. [b]%.

IV. Composite elemental wood analyses (2-4)

	Softwoods[a]	*Hardwoods*[b]
Macronutrients, %		
N	0.059	0.078
P	0.005	0.005
K	0.04	0.03
Ca	0.07	0.09
Mg	0.016	0.018
S	0.022	.015
Micronutrients, ppm		
Cl	100	50
Fe	27	20
Sl	170	215
Cu	1.4	1.4
Zn	17	12
Mn	150	100
Other elements, ppm		
Al	12	15
Na	50	70

[a]Scandinavian pine and spruce and northeastern U.S. spruce. [b] Scandinavian birch and northeastern US. hardwoods.



1. Flow of raw materials and products.

V. Amounts of elements in wood consumed and sludge produced daily

Element, kg/day	Amount in wood,[a] kg/day	Amount in sludge,[b] kg/day
N	2,310	4,104
P	165	492
K	1,122	275
Ca	2,706	6,145
Mg	561	928
Na	205	464
Al	46	384
Fe	68	590
Mn	96	22
Zn	46	22
Cu	5	11

[a]Based on 80% hardwood and 40% softwood (Table III) and 3,300 metric tons/day. [b]Based on average analyses for wood pulp mills and 199 metric tons of sludge/day.

having widely different applications in pulp and paper mills. Magnesium also had a wide range; it would be expected to be high in mills employing the magnefite pulping process. It appears that different mill operations can result in a wide range of element level.

Elemental composition of wood

Wood substance contains small amounts of mineral elements that have functions in wood growth. Elements required in relatively large amounts are nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur. Elements needed in smaller quantities are iron, manganese, zinc, copper, boron, molybdenum, and chlorine. Elemental compositions of typical northern softwoods and hardwoods, such as used in Wisconsin mills, are given in Table IV.

Amounts of elements in wood and sludges in pulp and paper system

The wood consumed in the wood pulp mills in this study represents quantities of the elements removed from the forest site on harvesting. Certain proportions of these elements appear finally in sludges from the treatment of the mill effluents. The sludges also contain certain portions of the chemicals present or added with the process water, pulping and papermaking chemicals, and effluent treatment. The flow of these chemicals in a pulp and paper system with the sludge provisionally recycled to the forest site is shown in Fig. 1. The daily amounts of the elements in the wood consumed and the sludge produced are given in Table V.

The courses of the individual elements in the pulp and paper system (from tree to sludges) are traced as follows (see also Tables III–V):

Nitrogen is an essential element in tree growth and is present in wood substance of the type used by Wisconsin pulp mills in the amount of about 0.07% (Table IV). Thus, the nitrogen in the 3300 tons of wood consumed daily in the pulp mills is 2310 kg. The major source of additional nitrogen is in the nutrient supplied in the biological treatment of the effluent. A small amount can enter the system as amides in waste paper, from the kraft recovery furnace, and in the treated effluent itself. The major part of the nitrogen appears in the sludge. In the present case, the amount of nitrogen in the sludge is 4,104 kg in comparison with the 2,310 kg derived from the wood.

Phosphorus enters the system in the wood but also enters in the processes of pulping and papermaking, especially as phosphates in detergents, for example. The latter amount is considerably in excess of that required in the secondary treatment of the mill effluent, and the sludge is relatively high in phosphorus.

Potassium is mostly introduced with the wood. A small amount is taken up by the pulp and an appreciable quantity is found in the bleach plant effluent. The bulk apparently is consumed in the secondary treatment (along with added potassium) with about 25% of the amount in the wood being present in the sludge.

Calcium is the most abundant of the wood mineral elements, but its contribution is overshadowed by the calcium added in the pulping and bleaching liquors. The. average amount of calcium contained in the sludges was over twice that contributed by the wood.

Magnesium enters with the wood in an appreciable amount. A large quantity is added to the system in magnefite pulping. This increases the magnesium average for the total sludge (Table V); otherwise, there was a consumption of the original wood magnesium of about 60% in the course of the flow in the pulp and paper system.

Iron has a low concentration in the wood, but the sludges show a high Fe content from corrosion from within the system.

Manganese is a minor element in wood and appears even less conspicuous in sludges because pulp absorbs it.

Zinc is another minor element in wood that appears to be consumed or lost in the system, in that the sludge contains only 40% of that contributed by the wood.

Cadmium is a nonessential plant growth element and very little is found in wood it may be toxic to plants and may be found in plant products. Cadmium can enter the pulp and paper manufacturing system through detergents, pigments, and plastics, including polyvinyl chloride. Cadmium compounds tend to concentrate in the sludge from the effluent treatment system. The toxicity of cadmium compounds has led to governmental guidelines to limit their presence in sludges used agriculturally, as discussed later.

Copper, on the other hand, is picked up along the route and is found to have increased considerably by the time it gets to the sludge.

Aluminum is moderate in quantity in wood but a large amount enters the effluent system from the clay coating and papermaking alum. Aluminum has the second highest content of the elements in the sludges.

Sodium enters the system in a moderate amount from the wood and during kraft pulping recovery make-up and bleaching chemicals. A considerable amount is absorbed by the pulp. The sludge shows a higher percentage of sodium than enters with the wood.

Sludge use

Landspreading. Pulp and paper mill sludges contain cellulosic fibers and chemical compounds of nitrogen,

Element	Paper mill, %	Municipal, %
N	2.9	10.5
C/N	26.1	...
Ca	2.95	6.1
Mg	0.46	0.9
Ca/Mg	6.4/1	6.8/1
Cu	0.007	0.05
Fe	0.29	0.9
Mn	0.028	0.02
B	0.001	0.03
Zn	0.01	0.24
Cd	0.0004	0.0026

See Literature cited, Ref. #7.

VI. Chemical elements in pulp and paper mill and municipal sludges

phosphorus, potassium, and other elements. They can serve to increase the water-holding capacity of soils (especially sandy soils), improve soil structure, and supply nutrients for plant growth. The nitrogen content of the sludge, for example, is most important in landspreading sludge. The annual nitrogen uptake for a hardwood–softwood composition in the proportion of 60/40 is estimated at 70 kg/ha (5). The nitrogen in the 70,000 tons of sludge produced in the studied mills at a content of 2.9% is 2,030 tons. Thus, the forest land area required for consumption of the sludge nitrogen, assuming a nitrogen-deficient sandy soil, would be 29,300 ha. The application in actual practice would be considerably higher, and the land requirement correspondingly lower. The forest land needed to support the daily wood requirement for the mills in this study of 3,300 metric tons (1.155 million tons annually at 350 days) at a nominal annual growth rate of 4 metric tons/ha would be about 290,000 ha.

An important measure of the suitablility of a sludge for landspreading agriculturally and silviculturally from the standpoint of its nitrogen content is its ratio of carbon to nitrogen (C/N). This ratio is an indication of the tendency of the material to release nitrogen, on the one hand, or, on the other, to immobilize it. The guideline is usually taken as being in the range of 20/1 to 30/1. The average for the composite sludge of this study was 26/1. Individual sludges ranged from 16/1 to 46/1. Another measure of the suitability of a material for landspreading for plant growth is the ratio of its contents of calcium to magnesium (Ca/Mg). It is generally understood that this ratio should be a minimum of 6/1. The composite sludge in this study has a Ca/Mg of 10/1. The individual sludges had a range of 1/1 to 16/1. Those with low averages might need to adjust by lime addition for individual applications.

The trace elements, chromium, lead, and mercury, were possibly higher in some instances than found in soils, but were considered to be well below toxic levels. Cadmium applications in sludges for agricultural use is limited by a Wisconsin governmental guideline to 0.5 kg/ha annually, starting Jan. 1, 1987 (6). The minimum land area for application of the total sludge in this study to meet this limit would be 514 ha. Cadmium uptake by trees and its implications are not known.

Given in Table VI is a comparison of certain elements in the composite combined pulp and paper mill sludge and a municipal sludge used for agricultural landspreading. The paper mill sludge has a lower order of concentration for trace elements than the municipal sludge.

Incineration. Economic combustion of pulp and paper sludges for disposal or energy recovery is dependent on their solids and organic contents. The latter determines the heating value of the sludge on a dry solids basis, as influenced by the inorganic or ash contents. A guideline for auto-combustion of a sludge is that it has a minimum of 30% solids and 1400 J/g (6000 Btu/lb) heating value (8). Another guideline is that a sludge should have an organic content of 66.5% (33.5% ash): the average for sludge in this study would require a total solids content of 32.5% to support combustion (9). The actual average was 21% (Table II). Thermal preconditioning of low-solids sludges by wet air oxidation has been proposed to improve dewatering toward achieving a total solids content of 40% or over (10).

Experimental

Collection

The first samples of combined primary/secondary sludges were collected in the winter of 1976–77at mills with early treatment facilities. Another sampling was made in March–April 1979 at five of the seven treatment plants eventually included in the investigation. The final sampling of 7 plants was made in Jan.–Feb. 1980 when the plants were understood to be under stable operation. The samples were collected over a period of about an hour when operation was reported as normal. Supplemental operating information was obtained at this time.

Analyses

The sludge samples were tested for solids and ash contents and pH by normal procedures and for carbohydrates by determining the total reducing substances (calculated as weight of glucose) in the filtrate by the Klason lignin procedure (*11*). Total nitrogen was determined by the Kjeldahl procedure, and the macro- and microelements and other elements were determined by inductively coupled plasma (ICP) spectroscopy.

The calculations for organic carbon and C/N are as follows:

% organic carbon = %organic matter/l.72
(organic matter = 100% – %ash)
C/N = % organic carbon/% nitrogen

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