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ALTERNATE METHODS FOR DISPOSAL
OF NITROCELLULOSE FINES

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and
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<p>An assessment has been made of current wastewater treatment capability at Army nitrocellulose propellant manufacturing facilities and the ability of these sites to maintain compliance with discharge criteria.</p> <p>A review of commercial wastewater treatment processes has shown that there are no directly comparable industrial problems. Other industries with problems of colloidal solids, such as phosphate mining, pigments manufacture, etc., use combinations of conventional technologies (coagulation, sedimentation, filtration) or have ponds where evaporation plays an important role. There is only one U.S. nitrocellulose manufacturer, and that facility discharges directly to the river just as Radford Army Ammunition Plant does and is in compliance just as RAAP is. Cellulose fines are not as small as NC fines and tend to incorporate into paper products when water is</p>						
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There are several "ready technologies" that appear to be capable of removing NC fines more thoroughly than current RAAP practice does: improved settling pit design probably combined with coagulation similar to that used in the paint and pigment industry; centrifugation; and of course combinations of these. These technologies could be implemented relatively quickly without any R&D program and could serve to keep RAAP out of trouble in event of increased production or moderately tightened discharge limits. It is recommended that RAAP prepare an engineering design and an implementation plan for these technologies to have on the shelf in event of need. It must be noted, however, that improved NC removal would generate new problems in the form of NC-rich sludges.

There are also at least 19 "innovative technologies" that might, with development, provide even more effective NC fines removal. These innovative technologies have been assessed and compared; and five of them - sticky filters, ion control, liquid/liquid extraction, crosslinking and laser pyrolysis - are recommended for exploratory development. Two other technologies - ultrafiltration and microfiltration - have seen extensive development in other fields and are recommended for engineering study.

This report presents the details of the technology assessment and comparison methodology, along with recommended exploratory development and test plans.

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TABLE OF CONTENTS

	Page
1. INTRODUCTION AND SUMMARY.....	1
2. WASTEWATER TREATMENT TECHNOLOGIES	
2.1 Ready technologies	
Centrifugation.....	2
Coagulation.....	3
Improved settling pits.....	4
Combined technologies.....	5
Water recycle.....	5
2.2 Innovative technologies	
Liquid/liquid extraction.....	6
Cross-linking.....	7
Dissolved air flotation.....	7
Ion control.....	8
UV-ozone oxidation.....	9
UV-ozone oxidation w/ultrasonics.....	9
Electrodialysis.....	10
Electro-osmosis.....	10
Electrocoagulation.....	11
Ultrafiltration.....	11
Hydroperm microfiltration.....	11
Biodegradation.....	12
Anaerobic biodegradation.....	13
Insect/enzyme systems.....	13
Sticky filters.....	13
Microwave.....	14
Plasma.....	14
Laser pyrolysis.....	14
Hydrogenation/hydrogenolysis.....	15
2.3 Ultimate disposal of NC solids	
General.....	17
Thermal degradation.....	17
Carver-Greenfield pyrolysis.....	18
Chemical conversion to useful products.....	18
3. TECHNOLOGY ASSESSMENTS	
3.1 Approach.....	19
3.2 Performance and cost criteria and weightings....	19
3.3 Matrix comparison of technologies.....	22
3.4 Ranking and selection of technologies.....	26
4. CONCLUSIONS AND RECOMMENDATIONS	
4.1 Conclusions.....	28
4.2 Recommendations.....	28
5. R&D PLAN	
5.1 Engineering of ready technologies.....	29
5.2 Exploratory development of new technologies.....	29
6. BIBLIOGRAPHY.....	35
APPENDIX.....	38

1.0 INTRODUCTION AND SUMMARY

Current facilities for treatment of NC fines-bearing wastewaters at Radford Army Ammunition Plant (RAAP) consist of settling pits, a bank of DeLaval centrifuges and, after mixing with other wastewaters, a final settling lagoon. The centrifuges are not being operated at this writing (spring 1985) because, at current production levels, RAAP is in compliance with their discharge permit without them. However, RAAP would probably not be in compliance at mobilization rates and would certainly not be in compliance if the discharge limits were to be significantly tightened. Accordingly, USATHAMA initiated this project to identify and assess alternate, more effective, methods of NC fines minimization, segregation and disposal.

A review of commercial wastewater treatment processes has shown that there are no directly comparable industrial problems. Other industries with problems of colloidal solids, such as phosphate mining, pigments manufacture, etc., use combinations of conventional technologies (coagulation, sedimentation, filtration) or have ponds where evaporation plays an important role. There is only one U.S. nitrocellulose manufacturer, and that facility discharges directly to the river just as RAAP does and is in compliance just as RAAP is. Cellulose fines are not as small as NC fines and tend to incorporate into paper products when water is recycled; and, being ubiquitous in nature, are not considered pollutants anyway.

There are several "ready technologies" that appear to be capable of removing NC fines more thoroughly than current RAAP practice does; improved settling pit design probably combined with coagulation similar to that used in the paint and pigment industry; centrifugation; and of course combinations of these. These technologies could be implemented relatively quickly without any R&D program and could serve to keep RAAP out of trouble in event of increased production or moderately tightened discharge limits. It is recommended that RAAP prepare an engineering design and an implementation plan for these technologies to have on the shelf in event of need. It must be noted, however, that improved NC removal would generate new problems in the form of NC-rich sludges.

There are also at least 19 "innovative technologies" that might, with development, provide even more effective NC fines removal. These innovative technologies have been assessed and compared; and five of them - sticky filters, ion control, liquid/liquid extraction, crosslinking and laser pyrolysis - are recommended for exploratory development. Two other technologies - ultrafiltration and microfiltration - have seen extensive development in other fields and are recommended for engineering study.

This report presents the details of the technology assessment and comparison methodology, along with recommended exploratory development and test plans.

2.0 WASTEWATER TREATMENT TECHNOLOGIES

Current (Spring 1985) treatment of wastewaters bearing NC fines at Radford Army Ammunition Plant (RAAP) consists of settling pits followed by centrifugation and some lagoon settling. The system could be upgraded considerably by the intensive implementation of several existing "ready technologies", but the addition of one or more new "innovative technologies" would be needed to meet significantly tightened discharge limitations.

2.1 Ready Technologies

Based on a review of the various technologies that have been tested and reported (see, for example, Final Report PE-221, April, 1974), primarily at and for Radford Army Ammunition Plant, and discussions with personnel at Radford and Picatinny, three approaches appear to offer immediate help in minimizing the NC fines problem. These three processes or approaches are (1) centrifugation; (2) coagulation; and (3) improvements in the poacher settler pits. Perhaps equally important would be combinations of these three concepts to maximize the benefits of each in terms of reduced nitrocellulose fines in the ultimate discharge. Limited work also has been done on other processes, including reverse osmosis and ultrafiltration; in addition to costs reportedly of the same order as those for centrifugation, these processes may encounter a problem due to membrane fouling or deterioration.

In addition, scrutiny of the literature suggests that the nitrocellulose fines most resistant to separation, particularly in the poacher pits, may be quite different from the bulk nitrocellulose product. Further in-depth investigation of the characteristics of the fines may be a fruitful route to defining the problem and may lead to improved means of removal from the wastewater stream. Such an investigation may also lead to a conclusion that the NC fines are so different from product NC that reuse or recycle as an explosive material ceases to be a viable or desirable option. Alternate use or destruction routes then would be required.

CENTRIFUGATION

Several different approaches to centrifugation have been considered and investigated for the removal of NC fines, including the nozzle centrifuge, the solid bowl centrifuge, and the DeLaval sliding bowl centrifuge. Initial screening work on NC fines with a nozzle centrifuge was encouraging, but this system was not practical for scale-up and emphasis then shifted to the DeLaval sliding bowl centrifuge. Extensive testing with a 1000 gph prototype of the DeLaval (Report PE-221, April, 1974) demonstrated that these centrifuges were capable of consistently reducing the residual NC fines in the wastewater from the poacher pits. The supernatant could be recycled to the recovered water storage tank with little or no build-up of solids while solids were concentrated to 1% to 3% solids. Unfortunately, the water wash needed to sluice the solids from the

solid bowl diluted the solids to a concentration of only 0.03 to 0.1% solids. Subsequent work demonstrated that the sludge from the DeLaval's could be further concentrated using a Bird solid bowl centrifuge. During this study it was also observed that the boiler pit effluent was much more readily separated by centrifugation than the poacher pit liquor, although both discharges could meet the APSA 25 ppm requirement. High variability in results with the poacher pit liquor may have been due to fluctuations in the solids content in the incoming wastewater and in its temperature.

Based on these results, a bank of DeLaval centrifuges was installed to service Radford's NC washwater lines. Due to the currently reduced production level, the centrifuges are in a stand-by mode from which they can be activated readily; we believe they should allow Radford to produce supernatant suitable for recycle or discharge to the final lagoon. From our consideration of the information we have reviewed on the centrifuges, it is suggested that the use of poacher pit water (or a separate, internal recycle stream) as centrifuge washwater would minimize the dilution being experienced. There appears to be no advantage to or need for fresh, filtered water at this point; in fact it would seem that the washwater should be as highly "contaminated" with fines as can be tolerated since this should also help subsequent settling of the sludge.

(Combining the centrifuges with the other two concepts being proposed could markedly improve the sludge solids content and the removal of NC fines from the poacher pit liquor. This will be discussed at greater length in the succeeding subsections.)

COAGULATION

Results reported by Wang and coworkers at Rensselaer (L.K. Wang, et al, 1976) and by investigators at Radford on the use of polyelectrolytes as coagulants for NC fines demonstrated that coagulation of NC fines can successfully remove the solids from the poacher pit discharge and produce an effluent meeting the APSA guideline of 25 ppm. However, we have been advised that the technique as tested at Radford was not considered cost-effective. Contamination with polymer also would probably preclude reuse. We have given these two problems or deterrents serious consideration and would like to offer "rebuttal" arguments.

First, we agree that the use of 100 ppm of costly polyelectrolytes, as studied by Wang and coworkers, would not be cost-effective. This level seems extraordinarily high. We could find no evidence that alternate, less costly means of achieving the same levels of solids removal, with the possible exception of the use of bentonite as a "weighting agent," were explored. For example, we find no evidence that alum, ferrous sulfate, etc. were tested as possible coagulants. Consequently, the customary combinations of coagulants and SMALL AMOUNTS of polyelectrolytes were also not investigated. These routes might produce the desired coagulation and allow improved clarification, at lower cost. Work at Badger AAP (G.K. Shalabi, PI-02, 12 Feb 1975) reports the successful use of alum to reduce suspended solids from NC manufacture; unfortunately, the results are only reported in terms of turbidity and a direct comparison cannot be made.

Second, initially we accepted the concept that coagulation was unattractive because it would make the recovered solids unsuitable for reuse/recycle. Delving further into the current status of the problem, we realized that the solids are not currently being recovered. Their continued loss can hardly be considered a disadvantage for any particular treatment option, albeit recovery and reuse would certainly be an advantage for any treatment process. In addition to the uncertain properties of NC fines reported by several researchers, changes in cellulose feed (cotton linters versus wood fibers) also may prevent the reuse of fines, even if recovered uncontaminated by flocculants. Certainly, if the recovered solids (contaminated with flocculants) are not reused, they will present an ultimate disposal problem and cost (e.g., landfill, caustic degradation, incineration) that must be factored into an overall treatment scheme. Before accepting the "ultimate disposal" option as a cost, USATHAMA should investigate alternate uses for the solids, in the commercial sector as well as by the military. In any case, it should be noted that even total removal of the 25 ppm NC fines from 2.4 mgd/line yields only 500 lb. of NC fines/day/line.

IMPROVED SETTLING PITS

It is difficult to know whether the design of the settling pits does or does not have a significant effect on the effectiveness of settling and, thus on the effectiveness of overall solids removal. Clearly, if a system were being newly designed to serve simultaneously as the poacher pit and as a "pretreatment" for the recovered water system, one would use a different structure to minimize variations in incoming waste, mixing, turbulence and even, if necessary, the effect of wind on the surface. Recognizing the very difficult nature of the NC fines (hydrophilicity, size, shape, etc.) such careful attention to design might be productive, particularly in the introduction of wastewater and in the placement and design of the overflow pipe.

From the results reported (PE-221) for tests with the centrifuge, an initial equalization basin appears to be a necessity to overcome variations in solids. Testing of solids content at different locations and depths within the existing pits would be a good first step in learning whether the suspected variability does exist. Subsequent studies to design a new clarifier system may depend, at least partially, on whether the centrifuge will be used or not. If space is a constraint, the benefits of lamellae-type separators could also be reconsidered.

Similarly, if the centrifuges are used in conjunction with these pits, maximum sedimentation becomes doubly important, both in the "primary" basin and also in the basin that receives the sludge discharge from the centrifuges. Segregation of the wastes into two or even three basins may be desirable: (a) raw poacher pit liquor, (b) centrifuge solids at 1-3%, and (3) supernatant from the centrifuges. The supernatant or centrifugate from the centrifuges, being the "clean" wastewater produced in the system, should be isolated from recontamination and should be suitable for use in

the recovered water system. Also, as noted earlier in the discussion of centrifugation, a wastewater rich in NC should be used to sluice the sludge from the centrifuges; this may be the influent to the pits, an underflow from some point within the (redesigned) poacher pits-clarifier, or a fourth, internal recycle stream.

Similar comments concerning optimization can also be applied to the final lagoons. Improved baffling, control of inlet and discharge points to assure against short-circuiting, and if necessary, improved pH control would all help to maintain consistent, low levels of suspended solids in the effluent. Other than cost, there would be no reason for not adding coagulants and polyelectrolytes to the lagoons if it significantly improved solids removal.

COMBINED TECHNOLOGIES

It would seem that the separation of NC fines from poacher pit liquor could be maximized by a combination of the above technologies. Thus, the introduction of coagulants (and polyelectrolytes) might be fruitless without a physical system allowing proper mixing, coagulating, and settling zones. Similarly, the introduction of coagulated solids/wastewater into the centrifuges might produce a quite different separation of solids and liquids, even depending on the strength of the flocs produced in the coagulation. And, if the influent to the centrifuges were a more concentrated underflow liquor/sludge from a redesigned clarifier, the results of centrifugation might be further improved with the production of a more concentrated sludge and/or a cleaner centrifugate. Consequently, while we suggest that each of these concepts be examined independently initially, the goal should be to combine any advantages that can be gained from each.

Water Recycle

While DOD has devoted considerable effort to the recycling of the wastewaters from NC manufacture (J.L. Evans and R.L. Dickenson, PE-290, Nov 1973), it appears that many of the suggested options have not yet been implemented. Since such routes present a second opportunity to isolate or concentrate NC fines, as well as to minimize water use and conserve the energy needed to heat the washwaters, more attention to such options would seem to be a cost-effective effort. The use of counter-current washing and rinsing should receive particular attention along with the substitution of recovered wastewater for as many of the washing cycles as possible as recommended by Evans and Dickenson. In considering these recycle options, a secondary goal would be minimum removal of fines, thus allowing maximum incorporation of the fines in the product. In fact, this may be an opportunity to reexamine the overall wash and rinse requirements of the NC process; modern scouring technology from the textile and pulp and paper industries may suggest accelerated washing schemes and thus, reductions in the amount of wastewater (and NC fines) requiring treatment.

2.2 Innovative Technologies

We have identified at least 19 innovative wastewater treatment technologies that might be applicable to NC fines wastewaters.

Liquid/liquid Extraction

The application of liquid/liquid countercurrent extraction to large-scale industrial separations dates from the early 1930s, when it answered the need for a method of removing aromatic hydrocarbons from the kerosene fraction during oil refining. Since then it has found everincreasing application in a wide range of industries from copper production to the manufacture of antibiotics, but applications to the cleanup of wastewaters is only just beginning. For example, it had been suggested for the removal of heavy metals in electroplating wastewaters.

In running an extraction, the two phases -- the feed stream to be extracted and the extractant -- are mixed thoroughly and then allowed to separate into two layers. The two layers are pumped off into two separate vessels, and one stage of liquid/liquid extraction is complete. In practice, a single, discreet, equilibrium, extraction stage is seldom used because the distribution coefficients are seldom high enough to make that practical; multi-stage, countercurrent extraction to give much higher effective distribution coefficients is more common.

One ordinarily thinks of extraction as using a solvent immiscible with the original carrier liquid, but it is just as valid to use an immiscible liquid with a high affinity for the material to be removed. In the case of suspended nitrocellulose fines, an immiscible liquid that would preferentially wet the fines would qualify as an extractant. A solvent would be even better, of course, and an attractive candidate would be Union Carbide's Flexol 4G0, tetraethylene glycol di(2-ethylhexoate). It is a primary plasticizer for NC, is soluble in water to less than 0.01% by weight at 20 C, is non-toxic and non-irritating, and is biodegradable. There is a good possibility of using the NC-loaded extract stream directly in nitrocellulose plastics or lacquer manufacture without any separation or recovery of solvent. The practicality is entirely a question of a suitable market and of the economics. There are, of course, a large number of other possible extractants in addition to the Flexol.

Economic recovery of the solvent and retention of residual solvent by the aqueous phase are two aspects that would require careful consideration. Clearly, the solubility in the wastewater must be very low, as reported for Flexol 4G0. The toxicity and/or biodegradability of the solvent also can be a factor in determining how complex the total process would be. For example, any solvent entrained in the wastewater would constitute a "secondary waste". On the other hand, the most attractive scenario would have the non-aqueous solvent phase/isolated nitrocellulose marketable in that "dope" form. If that cannot be achieved, then additional cost and chemical loss would be necessary to remove or replace the solvent. In any case, solvent losses usually must be considered a major cost item when using liquid/liquid extraction.

One unique approach which has only recently been receiving interest in waste treatment is the use of supercritical solvents such as carbon dioxide or butane. The latter solvent is used in petroleum recovery processes. In this approach, the second or new solvent is one which can be caused to enter the supercritical phase (between liquid and gas) by the application of high pressures. Once in the supercritical stage, the solvent must exhibit significantly improved solubility for nitrocellulose. Reducing the pressure below the supercritical pressure then would cause the solute, nitrocellulose, to come back out of solution -- as a dry solid. The solvent is then recycled by re-elevating the pressure. Although the initial reaction would be that this would be an extremely costly process, recent work on its use for the regeneration of carbon has demonstrated that a continuous system that is considerably more economical than expected and offers other advantages, at least in carbon regeneration, is possible.

Crosslinking

Essentially the basis for this concept already may have been demonstrated by the use of coagulant polymers. If the molecular weight of the fines can be increased, it should help the flocs/fines to settle or improve the ease of centrifugation. Analytical results (D.O. Helton, June, 1976) indicate that NC fines have higher levels of residual free hydroxylic groups than product nitrocellulose. If these are the result of hydrolysis during washing, this functionality may be susceptible to crosslinking with reagents typically used with other cellulosic products. Candidates of particular interest could be formaldehyde, dialdehydes, diacids, and diols. Formaldehyde, in spite of its suspected carcinogenicity, may be the most attractive candidate for use in the dilute aqueous medium of the poacher pit liquor, at least in preliminary testing. The increased solids potentially produced by such crosslinking would be expected to be significantly different from NC and thus would have to be very carefully studied before it were mixed with product NC. It is more likely that such solids would have to find uses outside the military explosives area or be disposed of by some other process.

The major advantage of this approach -- if it can be accomplished with nitrocellulose -- is that it could be done in dilute aqueous medium such as the wastewater. Clearly, excess crosslinking agent would be needed and would probably be lost in the wastewater. This could require subsequent treatment for this "secondary waste". Both capital and operating cost should be extremely low and the process could efficiently precipitate both NC solids and dispersed colloids of nitrocellulose that would be highly resistant to other isolation schemes.

Some work has been done on the crosslinking of NC in organic solvent solutions with divalent metals such as copper.

Dissolved Air Flotation

Air flotation was tried at Radford AAP in 1973 (see: "ADPA Meeting at Radford AAP -- Water Pollution Abatement and Control, 29 Jan 1974" and PE-221, April, 1974) but was deemed unsuccessful because the NC fines did

not attach to the air bubbles and separate as a coherent froth. Nevertheless, dissolved air flotation is widely used for other fine waste materials such as dyes and pigments and is worth further work. It should be possible to promote bubble attachment with suitable surfactants and wetting agents and/or agglomerating agents such as the Flexol 460 discussed above. At some ratio of plasticizer to wastewater, plasticizer-promoted dissolved air flotation begins to look like liquid-liquid extraction and vice versa; so the two processes should probably be studied together.

Air flotation is inherently an economical process widely employed in wastewater treatment, but the economics for this application remain to be determined. The amounts of additives required are not known, and the possibility of cost recovery through the use of the NC-rich froth in plastics or lacquer manufacture have not been explored. It is to be doubted that the NC-rich froth would be suitable for recycle into propellant manufacture. Consequently, disposal of this "secondary waste" would also be necessary.

DAF lends itself to continuous operation and with monitoring of the nature of the froth can be expected to operate efficiently with a minimum of supervision even while minor changes in process wastewater occur.

Ion Control

A number of brief, passing references to the effect of pH and salt content on the flocculation of NC fines were uncovered while searching the literature on nitrocellulose. These references suggested that these properties should be examined in depth as a means of controlling coagulation and settling. The obvious first step should be to examine the production and removal of fines at different pH levels in poacher pit liquor and boiler pit liquors.

Two opposing approaches to the control of ionic strength (and perhaps character) could then be investigated (J. Epstein et al, June, 1978). It is reported that both the removal of certain cations and the introduction of these same ions to much higher levels can improve the removal of NC fines. Such "salting out" is a well-known means of precipitating materials from solution. It would be most attractive to evaluate such approaches by simply testing increments of salts on portions of a single sample of waterborne NC fines. An alternate approach would be to evaluate processes such as dialysis and electrodialysis as means of segregating NC fines from the accompanying salts in a stock solution and then correlating the change in salt content and the success of NC fines settling or removal.

The opportunity to modify the ionic character of the wastewater enough to cause improved settling of the NC fines is extremely attractive since it would require very little capital investment or operating costs. Once the process has been developed, it should also lend itself to automated monitoring. Depending on whether pH adjustment or the introduction of cations (or anions) was selected, the precipitated NC fines

may be suitable for recycle as a propellant. The resulting, NC-free wastewater would have increased salinity or a pH that might require readjustment.

The alternate approach, removal of ions by, for example, osmosis, while being somewhat more complex, still offers similar low investment and operating cost while producing NC fines free of ions. The wastewater would also have reduced salinity -- but there also would be a concentrated saline waste from the treatment. Since no chemicals have been added to the wastewater, it may be possible to recombine the NC-free wastewater and this saline concentrate into a wastewater suitable for discharge.

UV-Ozone Oxidation

While NC is considered to be relatively stable to chemical oxidation under normal conditions and using conventional oxidants, there are reports that the material is sensitive to ultraviolet irradiation. Combining high intensity UV irradiation with an oxidant such as ozone may be particularly attractive for destroying the low concentrations of NC fines remaining, possibly after some form of "primary" solids removal. Several vendors now provide hardware capable of irradiating solutions even when they contain solids which would normally interfere with the penetration of the irradiation. Systems such as Westgate Research Corporation's "Ultrox" and TAFI's "ZOP" process have been examined for the treatment of TNT wastewater. Researchers also have demonstrated that other oxidants, such as hydrogen peroxide, also benefit by the use of UV irradiation, and that the wavelength of the irradiation may be particularly important (Zaleiko, unpublished). As part of any investigation, it may be useful to examine the reactivity of different NC fines, with different levels of nitration, to establish whether free hydroxylic groups are needed for oxidation.

Of course, any oxidative destruction such as with ozone, by degrading the NC to soluble species, does not offer an opportunity to recover nitrocellulose and may require further treatment to destroy soluble compounds. Nevertheless, such an approach would be particularly well suited to the treatment of dilute wastes such as the NC fines. Once the nitrocellulose -- and other oxidizable BOD and COD -- is destroyed, the treated wastewater should be quite acceptable for recycle. These processes are, however, relatively high in capital cost and do consume considerable energy. Even at NC levels of 10-25 ppm, operating cost would have to be carefully assessed.

UV/Ozonation with Ultrasonics

In addition to the well-documented UV-ozonation techniques, limited research has now been done on the incorporation of ultrasonics into this process for both the degradation of solids (e.g., sludge solids, tanning wastes) and the oxidation of soluble organics. There are indications that the processes are somewhat accelerated by the addition of the sonic element, as has also been observed for other chemical reactions. These combined techniques can provide continuous treatment, which could be

particularly attractive with a waste stream such as the poacher pit liquor and allow recycle of the treated liquor. In fact, ultrasonics alone may produce interesting results by physically dispersing or disrupting the fines or causing hydrolysis to soluble oligomers.

The use of ultrasound and the design of suitable systems is only in its infancy at this time, unfortunately. Because of the physical dispersion that may be achievable by sonication, the NC wastewater may be ideally suited for testing such an approach. Some reduction in necessary capital equipment may also be attainable by combining sonication with ultraviolet catalyzed oxidation.

Electrodialysis

As noted earlier, there is reason to suspect that control of the ionic strength and make-up of the liquor can affect the ease with which NC fines can be precipitated. In addition to the control of pH, removal of ions by dialysis, and addition of salts noted earlier, electrodialysis may be a "practical" way of implementing such a change in ionic character. If successful, the fines could be concentrated in one compartment of such a cell while salts produced in the other cells would be disposed. Since no additives are added, the concentrated NC fines could be acceptable for recycle. As with most membrane systems, a key factor will be whether a durable, non-fouling membrane exists or can be developed.

Cost, particularly capital cost, would probably be moderate, while the need to replace membranes could significantly increase operating cost. The isolated fines, being uncontaminated by salts or additives, should be acceptable for reuse. As in ion control, disposal of the dissolved salts should not present major problems.

Electro-osmosis

This process is relatively new to the US market, although it has been in the literature for a number of years (see C&EN, p. 23, Jan 1984). It has been used to concentrate/dewater coal mining wastes and has recently been described for the dewatering of phosphate mining slimes, which are similar to NC fines in that they are extremely fine and slow to settle. While its primary use seems to be in such sludge dewatering (and it might be used for NC fines in that manner, too) the technique is being proposed primarily to assist the coagulation of dilute NC wastewaters.

The process is relatively simple in design, consisting of a series of anodes and cathodes "judiciously" distributed around a basin or pond. Electrical current is passed through the solution, causing the solids to move toward one electrode due to the charge sphere they carry while the water moves out of the settling solids toward the opposite electrodes. It is our thought that the system could be incorporated directly into the existing pits; as such it would appear that both capital and operating cost would be rather low. Based on the available literature, it appears that the electrodes (usually iron) are gradually dissolved or corroded;

consequently, the settling NC fines would probably not be suitable for recycle unless inert electrodes (e.g., graphite) could be substituted. However, if the process is truly an "electro-osmosis" rather than "electrocoagulation" (as described below), then it should be possible to use non-sacrificial, inert electrodes -- which would not contaminate the supernatant wastewater.

Electrocoagulation

All indications are that the NC fines can be isolated from the wastewater by the addition of one or more coagulants or polyelectrolytes to neutralize the charge sphere surrounding each colloidal particle. Electrocoagulation seems to be very similar to electro-osmosis in that electrical current is passed through the wastewater by means of a series of electrodes. However, in this case, the process is dependent on the use of sacrificial electrodes of aluminum or iron to produce Al(III) or Fe(II) which then serves as the coagulating medium. The presence of ionic species (salts) in the liquor will help to assure relatively good conductivity in the solution. Electrocoagulation would cause the NC fines to agglomerate and either settle or adhere to the oppositely charged electrodes. Vibration of the electrodes may be sufficient to dislodge the particles. And, since the charge sphere would have been neutralized, a more dense, readily settleable or filterable sludge should be expected.

Although the addition of coagulants, by either chemical addition or electrocoagulation, would interfere with the reuse of the sludge, this process may be an attractive alternate means of introducing such coagulating agents into NC manufacturing wastewater.

Ultrafiltration

This process and the one following, Hydroperm, are suggested as two microfiltration techniques that should be able to remove very fine, difficult-to-settle solids from a wastewater. Previous efforts with ultrafiltration have been reported to be quite costly for NC manufacturing plants, in both capital and operating costs, probably due in part to the need for pressure to "drive" the process and partly due to the anticipated labor and cost involved in replacing membranes as they become fouled. The membrane replacement may be minimized by applying the process only to wastewater which has already been clarified by other conventional processes. That does, however, increase total cost and complexity. The concentrate sludge, while still containing considerable water, may be suitable for reuse since no chemical additives have been added.

Hydroperm Microfiltration

Hydronautics, Inc., of Laurel, MD manufactures a line of porous-wall filter tubes a few millimeters in diameter. In use, a slurry to be filtered is pumped through the tube at slightly elevated pressure and high velocity so as to flow in a turbulent mode; a filtrate is taken from the outside of the

tube as clear liquid percolates through the pores of the wall. The thickened slurry is re-cycled or pumped through a second filter tube for further concentration until it gets too thick to pump. The tubes are available in a variety of wall pore sizes, but 9 to 11 microns median is a popular size. Filtration is of the "cross flow" variety, which means that the turbulence tends to keep any filter cake from building up on the interior of the walls. The pores do slowly plug up, of course, and periodic backwashing is necessary. Hydroperm tubes have been successfully demonstrated in the filtration of suspended paint pigments and of hydrous oxides such as those from storage battery reclamation operations.

Hydroperm tubes have been considered for NC fines, but were judged to require too large an installation to be economical. A copy of the Hydronautics proposal and the government evaluation may be available in the ARDC files. It might be worth another look in combination with improved poacher pit settling or a partial centrifuge separation. Particular attention should be given to whether the available tubes will suffice or whether new, finer tubes will have to be manufactured.

Biodegradation

All indications are that NC and, presumably NC fines, are essentially insensitive to conventional biodegradation in aerobic wastewater treatment systems. Nevertheless, there are three approaches to biodegradation in the broadest sense that may be worthy of consideration.

The first and most conventional approach would be to attempt to develop a mutant bacterial culture capable of digesting NC fines, preferably in dilute aqueous solution. This would allow the wastewater, e.g., the poacher pit liquor, to be used as a feed stream to such a mutated treatment system. And, with the advent of bioengineering, it may also be possible to develop such a culture by these more elegant techniques. Modification of existing biological species to meet specific needs is being investigated or used by many industries. While a degree of such mutation might be achieved by careful acclimatization of conventional aerobic biological systems, more sophisticated changes may require such other techniques which are only now being developed. Admittedly, even if successful, such "engineered" bacteria probably would not produce degradation much faster than that found in conventional biological systems and disposal of a bio-sludge would have to be considered part of the process. That and the need for lagoons or "fermentation" reactors would be expected to increase the capital cost of such treatment significantly. One unusual concern that would also have to be considered is the effect of such bacteria in the vicinity of an NC plant and possible inadvertent decomposition of product NC in storage!

It should be noted, however, that there is no evidence at this time that such biodegradation could be achieved. Besides the uncertainty revolving about the development of such mutant strains, this approach would perform just as any conventional aerobic process.

Anaerobic Biodegradation

There is some evidence (Hibregste et al, 1978) that NC is anaerobically degraded slowly in landfills. Based on these results (plus increasing interest in anaerobic treatment in general), anaerobic treatment may offer a low cost option for the destruction of NC fines in dilute wastewater. Equipment and operating cost would be expected to be comparable to other biological systems. The possibility of secondary degradation products, as noted in the landfill study, which would require further treatment cannot be ignored.

Insect/Enzyme Systems

Admittedly, there is little basis for believing that a suitable insect, animal, or isolated enzyme system exists or could be developed that would be able to digest nitrocellulose. Nevertheless, since it would offer an opportunity to use existing species and their natural ability to degrade nitrocellulose (as, for example, termites or enzymes in termite stomachs degrade unnitrated cellulose), it holds forth the opportunity for an extremely inexpensive approach to destruction of NC fines in wastewater. Obviously, considerable experimental work would be needed to learn whether the residual, unnitrated functionality of NC fines was sufficient for such insect degradation or whether new species able to digest the nitrated form could be identified or developed.

Sticky Filters

In the area of air pollution control "sticky filters" are well known as a means of trapping particles. It is equally well known that in many cases filtration of liquids depends on the impingement of entrained solid particles on the filter bed, at least to produce deceleration. We propose that it may be possible to combine these two concepts by selecting a filter medium which, in addition to (or instead of) a torturous path for deceleration, offers an adhesive characteristic for the NC fines. One species that come to mind for this application is NC itself combined with a solvent or plasticizer which will soften or partially dissolve the surface of the filter particles of NC. This plasticizer could be added to the NC filter cake as a pretreatment or can be incorporated in the NC fines/wastewater. The fines would become incorporated in the filter cake and, while the cake would probably not be suitable for use in explosives because of the plasticizer, it may be perfectly acceptable for other, commercial uses. Alternatively, conventional filter media such as coal and sand might be pretreated by coating with a nitrocellulose lacquer containing sufficient plasticizer to produce the desired "sticky" surface.

The spent filter either could be reused as a filter medium, discarded, or, depending on the plasticizer, recycled to the process. The capital and operating cost for such a filter system, while more than that for a simple settling basin, should not be excessive. Alternatively, a deep filter bed of pre-plasticized nitrocellulose could be prepared and used until

excessive backpressure develops. At that time it would either be backflushed (not expected to be too successful) or replaced.

Microwave Thermal Degradation

The use of microwave heating has been examined for the disposal of hazardous wastes and found to have some promise. It is difficult to anticipate whether selective thermal degradation of the nitrocellulose could be obtained or whether the entire wastewater would simply heat up. Only if the former occurs would this concept have any potential. Even then, specific designs would be required for cost-effective treatment of NC wastewaters, via destruction of the nitrocellulose fines. It would also be necessary to study the resulting wastewater and ascertain whether any toxic or otherwise hazardous fragments are produced. The process would be expected to be quite energy intensive if the bulk water also had to be heated, even if not to the point of evaporation, as in incineration.

Plasma Thermal Degradation

Similarly, plasma heating of hazardous wastes has been effectively used for the destruction of concentrated hazardous wastes. As with microwave heating, new designs would be needed if a practical, cost effective system is to be developed. Considerable additional research would be needed to determine the effectiveness for treatment of dilute wastewaters and to evaluate the fragments produced.

Laser Pyrolysis

This is a conceptual process that has not actually been demonstrated as far as we know. The concept is to irradiate the water stream containing the NC fines with a high-power laser operating at a wavelength to which water is essentially transparent but at which NC strongly absorbs - perhaps about 3.5 microns or perhaps in the visible. If the power is high enough and the water transparent enough, the NC ought to reach pyrolysis temperatures before appreciable heat transfer to the surrounding water can occur, and decompose to small molecular fragments in situ. With suitable power inputs, the fragments ought to be water-soluble and biodegradable - or perhaps even CO, N₂ and H₂O. The process might be rather efficient, too; energy not absorbed by NC particles could be reflected back through again by mirrors (the laser mirrors themselves) so as to maintain the energy intensity at a high level, losing only what is actually absorbed.

The obvious wavelength of 10.6 microns (CO₂) is not recommended, because water has a strong absorption there; and neither is the 6 micron carbonyl band of NC because water absorbs near there.

Other than the laser itself, the treatment equipment would be absurdly simple: merely a transparent cell through which the wastewater stream flows on its way to the outfall. The windows constitute a problem: they must be both highly transparent and highly insoluble in water. Either quartz or Al₂O₃ might be suitable in the visible or in the near IR.

Hydrogenation/Hydrogenolysis

At a recent meeting, the concepts of hydrogenation (addition of hydrogen, reduction of oxygen functionality) and hydrogenolysis (hydrogenation plus hydrolysis of ester or ether linkages) were discussed. While such techniques would normally be extremely costly because of the need for high pressure equipment and the safety precautions required for the use of hydrogen, they have been presented in this report because of the dilute nature of the NC solution. It could be feasible to design a continuous system in which only a small volume of wastewater was treated per unit time, possibly even in the high pressure tubing itself (i.e., without an actual autoclave reactor). While hydrogenation or hydrogenolysis could solubilize the NC fines, secondary products would definitely be produced and subsequent treatment of these would have to be considered.

Another approach which is just beginning to be understood but which may allow a real breakthrough would be to take advantage of the high cavitation pressures developed in an ultrasonic generator. If such a system could be designed and if it could hydrogenolyze nitrocellulose to monosaccharide derivatives, it could be a relatively inexpensive means of destroying residual concentrations of nitrocellulose in wastewater. The resulting monosaccharide derivatives and other byproducts would have to be studied to assure that they were not toxic to the environment.

Several other innovative technologies were considered for treatment of NC fines wastewaters but were discarded as inapplicable to very dilute suspensions. The ones that received serious consideration are mentioned below as explanation to reviewers to whom they might occur as additional possibilities.

Carver-Greenfield Process

The Carver Greenfield dewatering process, while excellent for concentrating or dewatering a sludge once it has been separated from the bulk of the wastewater, is simply not suited to the dilute wastewaters which have been defined as the primary target of the current effort. Therefore, it has been removed from the list of those processes subjected to the ranking process.

In-situ chemical conversion

Similarly, most chemical conversion processes, in the sense of generating useful/useable products in commercial quantities by copolymerization, etherification, esterification, etc. of nitrocellulose, also have been recognized as not suitable for treatment of dilute wastewaters. Clearly, at the low NC concentrations present, a significant quantity of product is not going to be produced. Consequently, chemical conversion has been removed from the ranking matrix. However, it should be kept in mind that certain of these processes, e.g., hydrogenation, could solubilize the waste and thus meet that primary objective; these have been retained.

Incineration

Although incineration certainly has a place in the destruction of bulk NC wastes, the high energy required to evaporate water makes it unlikely that any form of this process could be cost- and energy-effective for the dilute NC-fines wastewaters. One conceivable exception could be the use of the wastewater to sluice bulk NC wastes -- or other PEP wastes -- into an incinerator.

2.3 Ultimate Disposal of NC Solids

Many of the proposed dilute wastewater treatment schemes result in isolating nitrocellulose fines contaminated by some other material (e.g., coagulant). The general concensus is that reuse of such material would not be looked on favorably by the military because of real or perceived hazards. If commercial uses cannot be developed, no option would remain but to collect and destroy these solids in a manner that would satisfy the DOD, the U.S. Environmental Protection Agency, and the state where the plant is located.

Four routes seem to have received attention for the disposal of fines and waste or off-spec nitrocellulose. These include caustic decomposition, thermal destruction (incineration), landfill, and open burning/detonation. Of these, only *incineration* appears to be acceptable in terms of today's hazardous waste management requirements. Caustic degradation is only partially effective, requires elevated temperature and careful control, and generates secondary pollutants requiring further treatment. Similar results and difficulties can be expected with aqueous ammonia (Wendt and Kaplan, 1976). Landfill disposal will simply not be acceptable for most wastes in the near future; experimental work with nitrocellulose has shown that the secondary pollutants in the leachate will require further treatment (K.R. Huibergste, 1978). Open burning also is no longer acceptable for environmental reasons. While encapsulation in anticipation of land disposal of the immobilized material has received some consideration, the results have not been promising in that either total immobilization was not achieved or reaction occurred between one of the components of the encapsulating material and the nitrocellulose.

THERMAL DEGRADATION

To date the various forms of thermal degradation remain the only techniques whereby elimination of any residual risk from bulk volumes of nitrocellulose can be assured. Considerable work has been done on the use and testing of various forms of incineration to accomplish this goal. Of the available systems, rotary kiln and fluidized bed incinerators appear to offer the greatest cost-effectiveness, based largely on operating costs (V.J. Ciccone et al, Sept 1978). More innovative destruction systems such as microwave or plasma degradation have not received enough study (and none with nitrocellulose) to allow reliable predictions to be made. The US EPA has been investigating these techniques with hazardous wastes (EPA 670/2-74-088, Nov 1974) and the DOD should keep abreast of this work so that a timely decision can be made about testing the processes on NC wastes. Wet air oxidation could be used but requires rather elaborate (and costly) equipment and offers no apparent advantage over more conventional incineration (R.S. Wentzel et al, April, 1982). Historical attempts to destroy nitrocellulose in sludge thermally while recovering calcium and/or acid values were not promising (PE-275); similar attempts in other industries have also been unsuccessful unless very large quantities of acid

were produced.

CARVER-GREENFIELD PYROLYSIS

The Carver-Greenfield process, in which an oil is used to dehydrate a sludge to a dry solid which is then pyrolyzed by heating in the absence of air, has been considered for a number of municipal and industrial wastes, particularly those that were thermally sensitive. In some cases, this process has offered economic advantages over incineration, even producing excess fuel value over that needed for decomposition. Unfortunately, it is difficult to predict whether it would have any promise with nitrocellulose wastes or whether the process could even be carried out safely with a material as unstable as nitrocellulose. Testing, on a small scale, would be necessary to test the process and its safety.

CHEMICAL CONVERSION TO USEFUL PRODUCTS

Another potential alternative to incineration of large quantities of NC-rich sludges could be chemical conversion to some product with commercial utility. Nitrocellulose lacquers immediately come to mind as attractive and requiring a minimum of processing (perhaps only dissolution in solvent) unless the higher levels of nitrate substitution in off-spec nitrocellulose interfere. These high levels of nitration also may make it difficult to convert this material to other derivatives without first carrying out a partial denitration. But, if this problem can be circumvented, other mixed derivatives possibly could be made by such reactions as polyethoxylation, acetylation, carboxymethylation, etc., using procedures as with cellulose itself. Hydrogenation/hydrogenolysis, as a potential source of oil-like liquids, is still another possibility (USBM, RI 8013, 1975). It is conceivable that entirely new cellulose derivatives with new and useful properties might emerge from a 6.1-type research program investigating such reactions. Of course, markets would have to be identified for any products resulting from such chemical conversions.

Finally, In examining any such chemical conversion options, it would be desirable to reexamine the means by which the waste was generated. Modifications of the waste treatment process could benefit the process used to produce the derivative while producing treated wastewaters suitable for reuse or discharge.

3.0 TECHNOLOGY ASSESSMENTS

In order to compare proposed innovative technologies (and available technologies, for that matter), some kind of systematic comparison and ranking system is needed. For this study, we have adopted the system used by another THAMA contractor, Environmental Science and Engineering, Inc., (Contract DAAK11-83-G-0303/0001, Nov. 1984) with some modifications to adapt it to the NC fines problem.

3.1 Approach

We have adopted the ESE approach of listing the key evaluation criteria deemed important for the particular problem, and ranking them in a weighted pair-wise fashion after the method of Motayed (ASCE, 1980). The criteria we have used are:

- o NC removal efficacy
- o Maturity of the technology
- o Tolerance to bad weather and upsets
- o Operating costs
- o Capital intensity
- o Labor intensity
- o Process complexity/simplicity
- o Worker safety
- o Energy intensity
- o Secondary wastes generated
- o Recovery potential

These criteria are defined and explained below as they pertain specifically to the removal of NC fines from RAAP wastewater.

3.2 Performance and Cost Criteria, and Weightings

The following eleven criteria were selected as the most pertinent and important to the removal of NC fines, with particular reference to operations at Army Ammunition Plants.

NC Removal Efficacy - This criterion represents the potential of removing the NC fines to an arbitrary low level in the outfall assuming the process works as projected. The process is not required to have been demonstrated, because that is considered under "maturity". Each technology is evaluated based on information available in the literature, experience in other treatment facilities, manufacturer claims, and project team experience and judgement. Note: Other important factors such as cost, safety, etc., are not considered here since they are evaluated separately.

Maturity of the Technology - This criterion refers to the demonstrated availability of the technology. Technologies that are readily available, off-the-shelf systems are rated higher than technologies that require a significant amount of research or development work. Included in this criterion are subjective estimates of the effort to take new technologies from the conceptual stage to the field.

Tolerance to Bad Weather and Upsets - Technologies with good tolerance of cold weather, wind, process upsets, or overload are rated higher than technologies with reported or suspected poor performance during less than ideal conditions.

Operating Costs - Annual outlays for labor, materials, maintenance, utilities, etc., but not including capital costs or amortization. Costs associated with further treatment of any secondary wastes are not included here.

Capital Intensity - Processes that require major up-front investments in plant equipment or construction are rated lower than processes that utilize existing equipment or require only minor investments.

Labor Intensity - This represents the degree of attention required from the operator or operators and the number of operators required, as well as the amount of manual labor required (particularly sludge handling) as distinguished from simply monitoring the operation.

Process Complexity/Simplicity - This represents the ease of operating the treatment process and of maintaining the equipment. The required skills of the personnel are considered, as well as the degree of sampling, monitoring and fiddling necessary to control the process. Complex, multistaged processes are ranked lower than single-stage, less complex processes.

Worker Safety - This encompasses the nature of materials and operations used in the treatment process. Processes that use flammable materials or high pressure, for example, are rated lower than those that operate at normal conditions or do not use dangerous materials.

Energy Intensity - Processes that require large amounts of heat or fuel or electricity are rated lower than processes that require less energy or actually yield energy as from the burning of sludge or methane. Note that wet NC sludge is not a net source of energy.

Secondary Wastes Generated - Many waste disposal operations in turn generate sludges or wastes of their own. The volume and problems of such waste products are considered. For example, processes that generate little or no sludge are rated higher than those that generate large volumes of sludges or hazardous wastes.

Recovery Potential - Processes that generate a useful product instead of a problem sludge, or that generate recyclable water instead of discharge water are favored.

The eleven performance and cost criteria defined above were compared, pair-wise, to each other by a panel consisting of the staff of John Brown Associates. We considered, for example, whether operating cost was more or less critical than capital intensity; whether operating cost was more or less critical than worker safety; whether tolerance to bad weather and upsets was more or less critical than operating costs - and so on through the entire matrix, pair by pair.

The pair-wise comparisons and rankings are given in the chart on the next page. In this chart, a "1" in a box means that the criterion at the head of the column is more important than the criterion at the left of the row; a "½" means that they are equally important or at least that we could not choose between them; and a "0" means that the criterion at the head of the column is less important than the criterion at the left of the row.

The pair-wise scores for each criterion were then totaled for each column (column, not row, since we wanted a *merit* rating for each criterion); and the merit ratings were normalized to make the best rating equal to 100. The normalized scores give the weighted ranking of each criterion relative to all the rest.

The net result is the following importance ranking of all the performance and cost criteria:

<u>CRITERION</u>	<u>WEIGHTING</u>
Worker safety	100
NC removal efficacy	80
Tolerance	75
Capital intensity	70
Operating cost	55
Secondary wastes	55
Process complexity/simplicity	45
Maturity of technology	30
Recovery potential	30
Labor intensity	10
Energy intensity	0

These rankings make sense. Worker safety is paramount - as always - and ability to do the job comes next, followed by major cost factors and then by secondary considerations.

At the same time, it must be appreciated that the rankings depend entirely on the judgements and priorities of the people making the pair-wise comparisons rather than on any objectively measurable, fundamental considerations. We believe that our judgements and priorities are sound, but it is always possible that the people who have to make final decisions may have different judgements and priorities; for example, they may consider capital outlay more important than tolerance to upsets, labor intensity more important than secondary wastes, or recovery potential more important than tolerance. Consequently, we recommend that decision-makers review our judgements and priorities for themselves; and that is why we have presented our methodology in such detail.

3.3 Matrix comparison of technologies

The same matrix methodology was also used to rank the various candidate technologies by comparing *them* pair-wise with each other in eleven separate matrices, *i.e.*, one for worker safety, one for operating cost, and so on, and then applying the weightings derived earlier. For these comparisons, we used an expanded panel consisting of Drs. Skovronek and Brown plus two consultants of broad wastewater treatment experience: Irving Forsten, formerly Chief of the Special Technology Branch, Manufacturing Technology Division, ARRADCOM, where he managed a multifaceted program that included all aspects of wastewater treatment at Army Ammunition Plants; and Paul Cheremisinoff, Professor at the New Jersey Institute of Technology and author of numerous books on industrial wastewater treatment. As before, the more desirable technology received a rating of "1" and the less desirable technology a rating of "0". Equally desirable technologies each got a rating of " $\frac{1}{2}$ ". The eleven pair-wise comparison matrices are given in the appendix.

Next the ratings for each process against each criterion were collected in a grand matrix shown on the next page. In this matrix, the higher the number in the chart, the more attractive the process by the criterion at the head of that column.

Finally the raw scores in the grand matrix were multiplied by the weighted values of the performance and cost criteria to give weighted figures of merit in each box; and the weighted figures of merit were totalled across the page to give a grand weighted figure of merit for each process as judged by *all* of the criteria. The outcome is a list of the treatment processes ranked in order of their relative attractiveness from the most attractive to the least attractive (page 25).

	NC REMOVAL EFFICACY	CAPITAL INTENSITY	OPERATING COST	MATURITY OF TECH	PROCESS COMPLEXITY	TOLERANCE	SECYRY WASTES	ENERGY INTENS	LABOR INTENS	RECOVERY POTENTIAL	WORKER SAFETY
NC REMOVAL EFFICACY	-	0	0	0	0	0	½	0	0	½	1
CAPITAL INTENSITY	1	-	0	0	0	1	0	0	0	0	1
OPERATING COST	1	1	-	0	½	1	0	0	0	0	1
MATURITY OF TECH	1	1	1	-	1	1	1	0	0	0	1
PROCESS COMPLEXITY	1	1	½	0	-	1	1	0	0	0	1
TOLERANCE	1	0	0	0	0	-	½	0	0	0	1
SECONDARY WASTES	½	1	1	0	0	½	-	0	0	½	1
ENERGY INTENSITY	1	1	1	1	1	1	1	-	1	1	1
LABOR INTENSITY	1	1	1	1	1	1	1	0	-	1	1
RECOVERY POTENTIAL	½	1	1	1	1	1	½	0	0	-	1
WORKER SAFETY	0	0	0	0	0	0	0	0	0	0	-
TOTAL SCORE	8	7	5½	3	4½	7½	5½	0	1	3	10
NORMALIZED SCORE	80	70	55	30	45	75	55	0	10	30	100

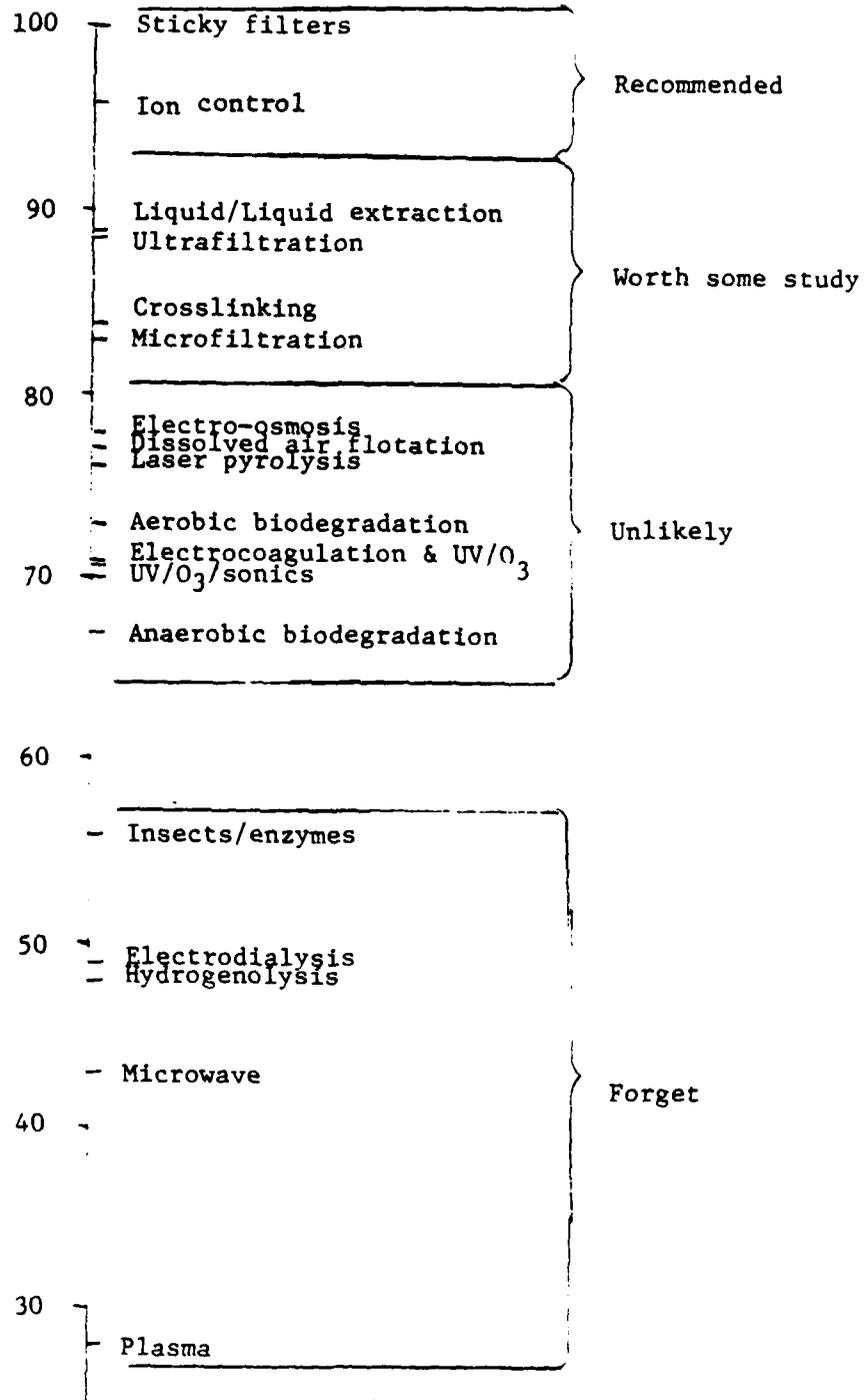
MERIT SCORES OF INNOVATIVE PROCESSES AS EVALUATED
AGAINST EACH PERFORMANCE OR COST CRITERION

	Worker safety	Removal efficacy	Tolerance to upsets	Capital intensity	Operating cost	Secondary wastes	Process complexity	Maturity of technology	Recovery potential	Labor intensity	Energy intensity
Liq/Liq	81	67	94	40	32	47	67	100	100	70	67
X-linking	100	46	41	94	62	47	81	18	42	58	89
DAF	72	61	56	57	56	47	39	100	39	42	64
Ion Adjust	94	64	68	100	79	47	78	44	39	58	86
UV/Ozone	22	88	68	23	21	100	64	85	39	94	19
UV/Ozone/Sonics	22	94	74	17	21	100	56	56	39	94	19
E-dialysis	50	27	24	46	44	31	19	71	39	6	33
E-osmosis	38	52	53	69	62	50	89	74	94	64	33
E-coagulation	38	58	53	63	62	50	69	68	36	52	33
Ultrafiltration	59	100	88	40	62	50	39	100	97	18	50
Microfiltration	66	64	88	40	62	50	39	82	97	18	58
Aerobic Degrad.	97	61	29	69	100	3	22	35	42	24	75
Anaerobic Degrad.	97	21	9	77	100	3	19	38	94	24	100
Insect/Enzyme	97	6	3	86	100	3	17	3	16	12	89
Sticky Filters	81	100	79	74	85	50	56	56	94	27	72
Microwave Pyrolysis	22	6	32	6	9	100	94	9	36	100	3
Plasma Pyrolysis	6	6	32	0	9	100	0	15	36	88	3
Hydrogenolysis	3	79	26	14	18	81	6	32	97	88	44
Laser Pyrolysis	25	39	100	66	24	100	100	26	36	100	11

<u>RANK</u>	<u>PROCESS</u>	<u>GRAND WEIGHTED FIGURE OF MERIT</u>
1	Sticky Filters	100
2	Ion Control	96
{3	Liquid/Liquid Extraction	89
{3	Ultrafiltration	89
4	Cross-linking	84
5	Microfiltration	83
6	Electro-osmosis	78
7	Dissolved Air Flotation	77
8	Laser pyrolysis	76
9	Aerobic Biodegradation	73
{10	Electrocoagulation	71
{10	UV/ozone	71
11	UV/ozone/ultrasonics	70
12	Anaerobic Biodegradation	67
13	Insects and/or enzymes	56
14	Electrodialysis	49
15	Hydrogenolysis	48
16	Microwave	43
17	Plasma	28

3.4 Ranking and selection of technologies

Plotted graphically, the candidate technologies resolve themselves into four groups:



Sticky Filters and Ion Adjustment are the clear winners, and an R&D plan for their development and application is presented in Section 5.

The four processes in the next group are recommended for some further study, since it is felt that their perceived shortcomings may disappear with a little work and that would put them in the top category. Liquid/Liquid Extraction would have been ranked in the first group if its efficacy had actually been demonstrated, and so would Crosslinking; so some benchtop work is in order. Ultrafiltration clearly will work, but its perceived capital costs are high and should be confirmed by engineering study. Microfiltration is virtually the same as ultrafiltration, but it needs to be confirmed that its larger filter pores will do the job on NC fines.

Laser pyrolysis is also recommended for some experimental work in spite of its low ranking in the matrix. Its low ranking is mainly because there is no experimental evidence that it would work; but if it were to work, it would be extremely attractive since it would produce no sludge or secondary wastes, require no materials handling and require only the simplest of process equipment (other than the laser itself).

4.0 CONCLUSIONS AND RECOMMENDATIONS

A number of specific conclusions and recommendations flow from the above data and comparisons.

4.1 Conclusions

1. The installed wastewater treatment at RAAP could be operated to produce effluent containing lower levels of NC fines than it currently is, but there is little or no incentive to upgrade it at present since RAAP is currently in compliance with their discharge permit.
2. Intensive implementation of existing, demonstrated technologies would probably keep RAAP in compliance at higher production levels but possibly not at mobilization level. They would not keep RAAP in compliance if discharge standards were to be tightened significantly.
3. No better cleanup technology has been demonstrated for NC fines anywhere in private industry.
4. There are at least 19 innovative technologies that have potential for more effective cleanup of NC fines. They range from demonstrated on other suspensions to highly speculative.
5. Five of the innovative technologies are worth an exploratory development effort to apply them to NC fines.

4.2 Recommendations

1. Carry out experimental and engineering design work, and prepare a detailed implementation plan for the three ready technologies - centrifugation, coagulation and settling - with a cost/benefit comparison, to have them quickly available in the event of suddenly increased production and also to serve as a baseline for more innovative technologies.
2. Carry out exploratory development, up to the pilot plant stage, of the five most promising innovative technologies to position them for adoption in the event of tightened regulations.
3. Initiate a study of processes for the ultimate disposal of concentrated NC sludges and wastes resulting from wastewater treatment operations.

5.0 R&D PLAN

Two complementary R&D plans are recommended, one to prepare for near-term requirements, and one to prepare for far-term requirements.

5.1 Engineering of ready technologies

There are three categories of technologies that are well beyond the research stage and available for engineering implementation:

- o The stand-by ~~RAAP~~ processes of coagulation, settling and centrifugation.
- o ~~Ultrafiltration or microfiltration.~~
- o Water recycle/re-use.

These processes all need some - but only a little - engineering study and cost estimation. Such study and estimation is outside the scope of this report, and it is recommended that THAMA have it done by an engineering or an operating contractor. An overview discussion of what might be done is given in Section 2 of this report.

5.2 Exploratory development of new technologies

This section considers the two top-rated innovative technologies, two from the second-rated group, and on third-rated technology that would be top-rated if feasibility were shown.

A single wastewater should be used for all these tests or at least for each series of tests to avoid any confusion from changes in the wastewater composition. Ideally, it should have been subjected to pretreatment/clarification so that it contains approximately 25 ppm nitrocellulose fines. Because of concerns about differences in chemical and physical properties of NC fines and product NC, wastewater reconstitution from solids would not be considered representative. In addition to total suspended solids and/or turbidity, at least pH, and salinity or conductivity should be measured on the wastewater.

Sticky filters

Task 1 - Experiment, using filter flasks and Buchner funnels, with porous filter media such as sand, diatomaceous earth or fiber mats wetted with a sticky liquid with an affinity for nitrocellulose. Examples of such liquids might be a commercial nitrocellulose plasticizer such as Union Carbide's Flexol 4GO, tetraethylene glycol di(2-ethylhexoate), which is a primary plasticizer for NC, soluble in water to less than 0.01 Wt-%, non-

toxic and biodegradable; or a white oil such as Exxon's Isopar H whose water solubility is approximately 20 ppm and which is also non-toxic and biodegradable; or perhaps a soft asphalt or a coating of algae. Determine optimized bed depths, flow rates, liquid loading, etc., for each system. Alternate porous media that would minimize the filter cake disposal problem might be crushed coal, paper mats or mats of NC fibers that could be burned at the burning grounds, or in an incinerator or perhaps even in the power boiler.

Task 2 - Determine the lowest level to which the NC fines in the effluent water can be reduced using (a) practical operating conditions and (b) best possible operating conditions.

Task 3 - Determine the degree to which the effluent water becomes contaminated with the sticky liquid; and assess the problems, if any, posed by that contamination.

Task 4 - If the process looks promising after the glassware stage, repeat the optimum conditions in larger apparatus with engineering similitude to full-scale equipment to confirm the process efficacy. Measure or estimate power consumption, plant equipment size, effluent water quality, sticky liquid losses, and capital and operating costs. Re-assess the ultimate disposal aspects of the filter cake.

Task 5 - Draw up a Level One process flow chart showing sizes of vessels, pumps, piping, etc.; and estimate capital and operating costs for a 1,000,000 mgd water treatment plant.

Liquid/liquid extraction

Task 1 - Experiment, using separatory funnels, with liquid/liquid counter-current extraction of fresh NC-fines-bearing water with candidate extractants such as Flexol 4G0 or other primary NC plasticizers, or with white oil containing adhesion-promoting surfactants. An integral part of this task is a literature survey of candidate plasticizers and surfactants selected for maximum NC affinity, minimum water contamination and losses, and minimum cost.

Task 2 - Determine the lowest level to which the NC fines in the effluent water can be reduced using (a) practical operating conditions and number of stages and (b) best possible conditions and the maximum practical number of stages.

Task 3 - Determine the degree to which the effluent water becomes contaminated with the extractant; and assess the problems, if any, posed by that contamination.

Task 4 - If the process looks promising after the separatory funnel stage, repeat the optimum conditions in a benchtop column with engineering similitude to full-scale plant extraction columns to confirm the NC removal efficacy and to measure or estimate power consumption, plant equipment size, effluent water quality, extractant losses, and capital and operating costs.

Task 5 - Address the question of disposal or reclamation of the spent extractant. Can it be sold with its NC? Distilled and recovered? Burned as fuel? What are the corresponding costs and handling problems?

Task 6 - If all is promising, draw up a Level One process flow chart showing sizes of vessels, columns, pumps, piping, etc.; and estimate capital and operating costs for a 1,000,000 mgd water treatment plant.

Laser pyrolysis

Task 1 - Survey available laser systems, including military lasers, for one with high power output at a wavelength to which water is transparent and at which solid NC absorbs. Water is transparent throughout the visible and out to about 2 microns in the infrared, and from about 3.5 microns to about 6 microns. NC has a strong resonant absorption at about 3.5 microns, and solid particles will intercept almost any wavelength without any need for bond resonance. One might consider a neodymium laser with its 1.06 micron output, or a ruby laser with its visible red output. One wants a Q-switched system for its very high power density in order to heat the NC particle to pyrolysis temperature before the induced heat can be conducted away by the water. SECRET security access would greatly expedite the search for a suitable laser; it is possible that a GFE military laser might be suitable and available for Task 2.

Task 2 - Given a suitable laser, irradiate samples of NC-bearing water with very short, very high power density, light pulses; and determine whether flash pyrolysis in a water environment is possible. Suitable equipment would be small quartz cells and whatever laser can be obtained.

Task 3 - If the concept works at all, widen the scope to other lasers, or perhaps special lasers, and more realistic equipment sizes. Assess whether the concept has any practicality as an industrial scale process; and if so, draw up a proposed development plan.

Ion control

There is essentially no experimental data to use as a basis for a test plan on any form of ion or pH control. Consequently, the first phase of the proposed work plan will be to carry out bench scale tests using techniques similar to those used to test flocculants.

PHASE I -- Bench Scale Tests

Task 1 - pH Adjustment - A "jar test" apparatus would be ideal for these tests. Increments of dilute (6N) sulfuric acid or sodium hydroxide should be stirred into aliquots of wastewater to provide 0.5 pH increments from about 5.0 to 9.0. After stirring for a uniform length of time, the solutions are observed for clarity, formation of flocs, settling of flocs, etc.

From the first set of tests, the most promising pHs should be selected and the test repeated within a narrower pH range to try to pin down the optimum level.

Task 2 - Salt additions - Using similar aliquots and the same jar test apparatus, increments of concentrated sodium chloride (e.g., 10% NaCl) should be added to increase the salinity of the wastewater in stages of perhaps 25% of that present originally until a five-fold increase has been achieved. As before, the solutions should be observed for clarity and floc formation.

Repeat using other *soluble* salts containing ions already present in the wastewater, such as calcium chloride, sodium sulfate, sodium carbonate.

Further tests should also be done with wastewater containing higher levels of NC -- and from different sources in the washing process -- to determine whether ratios or specific levels of additive are the determining factors.

Task 3 - Salt removal tests - For bench scale purposes, the simplest approach appears to be the use of dialysis membranes (cellulose sausage casings). Aliquots of NC wastewater are placed in sausage casings, sealed at both ends, and flooded with water for 24 hours or longer. As the dialysis occurs, the salts pass out of the wastewater to the more dilute water. Initially, it will only be necessary to observe the casing after several hours to see if larger flocs of solids are forming and, ideally, settling. Several samples can be immersed simultaneously, removed after different time increments, and tested for TSS/turbidity, pH, salinity, etc.

More sophisticated dialysis experiments can be carried out using small scale dialysis equipment and sheet membranes. Tests at several different pH levels may also be necessary to optimize the settling or coagulation of fines.

Task 4 - Sludge settling rates - Once promising pH levels, salt additions, or dialysis conditions have been identified and optimized to the extent possible in jar or bench scale tests, further differentiation may be achieved by measuring sludge settling rates in an Imhoff Cone or a graduated cylinder.

Gravity or suction filtration tests using paper filters also may give some indication of the plugging tendency of the sludges.

PHASE II - Pilot Scale Tests

Task 1 - Chemical additions - The best of the foregoing test results should be used as the basis for larger scale experiments from which additional information can be obtained concerning rates of addition, times for settling, and character of the sludges. A new lot of NC wastewater should be selected for this effort and analyzed for TSS and/or turbidity, pH and salinity or conductivity. It may also be desirable to know the concentration of specific

ions, such as sodium, calcium, chloride, sulfate, etc. Depending on availability, pH or specific ion meters or continuous turbidimeters may be very useful in providing immediate results and allowing "feedback" loops for controlling chemical addition. They would also facilitate the use of a slipstream from any desired point in the actual wastewater treatment system in the plant instead of a batch reservoir.

The system envisaged consists of a supply of NC wastewater which can be gravity fed solution to a mixing chamber where acid, base or salt would be metered in. In full scale operation, this could be achieved by in-line mixing. From the mixing chamber, the liquor would flow to a settling tank equipped with an adjustable overflow pipe.

Acid, base or salt would be added, either at some constant rate or in response to one or more electrodes in the mixing chamber -- or the settling basin. Quality of the clarified overflow should be measured either by grab samples or by continuous turbidity measurements. Once steady state conditions have been established, the wastewater flow rate can be increased until the quality of the effluent begins to deteriorate. Settling time can also be reduced by adjusting the depth of the overflow pipe. In any case, it should only be necessary to maintain records of feed rate, additive rate, overflow rate and the necessary characteristics of the overflow (pH, salinity, TSS/turbidity).

Task 2 - Dialysis - Various plate and frame dialysis cells can be used for pilot scale testing. Recirculating the wastewater through such a cell and monitoring the TSS or turbidity of the (intermediate) discharge should provide information such as flow rate/unit area of membrane needed to design a full scale system capable of treating a specified volume of wastewater/day to a preselected effluent quality such as 10 ppm TSS. Some indication of membrane fouling/plugging would also be gained from such tests.

Since the pilot scale program will also generate a quantity of sludge, it may also be useful to carry out filtration tests at this stage using a leaf filter. The change in filtration rate will be useful in determining whether filtration can be used to dewater the sludge if that proves to be necessary.

Cross-Linking

Certain reagents appear to offer the greatest promise for cross-linking the residual hydroxylic groups in NC fines in dilute aqueous solution. Of these, formaldehyde is the most attractive and the work plan that follows will use that material as the model compound. Other agents that should be considered, however, at least in the initial phase, would be diamines such as ethylene diamine, propylene diamine, hexamethylene tetramine and melamine + formaldehyde.

PHASE I - Bench Scale Tests

Task 1 - Using 40% formalin as the agent, initial "jar test" experiments should be carried out with a nitrocellulose monomer to formaldehyde molar ratio of perhaps 1:0.01; 1:0.05; 1:0.1; 1:0.5; and 1:1. Such a range of ratios assumes that the nitrocellulose fines contain a residual free hydroxyl concentration of much less than 1 per anhydroglucose unit.

Task 2 - Using the most attractive ratios, mixing times, and settling times, settling rates can then be determined in an Imhoff Cone or a graduated cylinder. Tendency to blind filters can be predicted by gravity or suction filtration through paper.

PHASE II - Pilot Scale Tests

Using the pilot scale equipment as described in the "Ion Control" section, larger scale, continuous cross-linking tests can be carried out to evaluate formaldehyde/NC ratio, pH, etc. that are best for the continuous system. In cross-linking, only TSS or turbidity can be used to monitor the progress of the crosslinking and coagulation/sedimentation.

Treatment of more concentrated NC wastewaters from other stages in the washing sequence should also be examined, particularly if the NC fines from that point are not being reused. This would avoid costly sequential treatment and might actually be more effective by providing a larger matrix (the solids) for cross-linking and co-precipitation.

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APPENDIX

(The eleven criteria matrices, individually.)

USE FOR WORKER SAFETY CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	1	0	0	0	0	0	0	0	0	0	1	1	1	1	0	0	0	0
Cross-linking	0	-	0	½	0	0	0	0	0	0	0	½	½	½	0	0	0	0	0
Dissolved Air Flot.	1	1	-	1	0	0	0	0	0	0	0	1	1	1	½	0	0	0	0
Ion Adjust	1	½	0	-	0	0	0	0	0	0	0	½	½	½	0	0	0	0	0
UV/Ozone	1	1	1	1	-	½	1	1	1	1	1	1	1	1	1	½	0	0	½
UV/Ozone/Sonics	1	1	1	1	½	-	1	1	1	1	1	1	1	1	1	½	0	0	½
Electro dialysis	1	1	1	1	0	0	-	0	0	1	1	1	1	1	1	0	0	0	0
Electro osmosis	1	1	1	1	0	0	1	-	½	1	1	1	1	1	1	0	0	0	½
Electro coag	1	1	1	1	0	0	1	½	-	1	1	1	1	1	1	0	0	0	½
Ultra filtration	1	1	1	1	0	0	0	0	0	-	1	1	1	1	½	0	0	0	0
Micro filtration	1	1	1	1	0	0	0	0	0	0	-	1	1	1	½	0	0	0	0
Aerobic Degrad	0	½	0	½	0	0	0	0	0	0	0	-	½	½	½	0	0	0	0
Anaerobic Degrad	0	½	0	½	0	0	0	0	0	0	0	½	-	½	½	0	0	0	0
Insect/Enzyme	0	½	0	½	0	0	0	0	0	0	0	½	½	-	½	0	0	0	0
Sticky Filter	0	1	½	1	0	0	0	0	0	½	½	½	½	½	-	0	0	0	0
Microwave	1	1	1	1	½	½	1	1	1	1	1	1	1	1	1	-	0	0	½
Plasma	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-	½	½
Hydrogen.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	½	-	1
Laser pyrolysis	1	1	1	1	½	½	1	½	½	1	1	1	1	1	1	½	½	0	-
TOTAL	13	16	11½	15	3½	3½	8	6	6	9½	10½	15½	15½	15½	13	3½	1	½	4
NORMALIZED	81	100	72	94	22	22	50	38	38	59	66	97	97	97	81	22	6	3	25

USE FOR NC REMOVAL EFFICACY CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	1/2	0	0	1	1	0	0	1/2	1	1/2	1/2	0	0	1	0	0	1	0
Cross-linking	1/2	-	1	1/2	1	1	1/2	1	0	1	1/2	1	0	0	1	0	0	1	1/2
Dissolved Air Flot.	1	0	-	1/2	1	1	0	1/2	1/2	1	1/2	1/2	0	0	1	0	0	1/2	0
Ion Adjust	1	1/2	1/2	-	1	1	0	0	1/2	1	1/2	1/2	0	0	1	0	0	0	0
UV/Ozone	0	0	0	0	-	1	0	0	0	1/2	0	0	0	0	1	0	0	1/2	1/2
UV/Ozone/Sonics	0	0	0	0	0	-	0	0	0	1/2	0	0	0	0	1	0	0	1/2	1/2
Electro dialysis	1	1/2	1	1	1	1	-	1	1	1	1	1	0	0	1	0	0	1	1
Electro osmosis	1	0	1/2	1	1	1	0	-	1/2	1	1	1/2	0	0	1	0	0	1	0
Electro coag	1/2	1	1/2	1/2	1	1	0	1/2	-	1	1/2	1/2	0	0	1	0	0	1/2	0
Ultra filtration	0	0	0	0	1/2	1/2	0	0	0	-	0	0	0	0	1/2	0	0	0	0
Micro filtration	1/2	1/2	1/2	1/2	1	1	0	0	1/2	1	-	1/2	0	0	1	0	0	1/2	0
Aerobic Degrad	1/2	0	1/2	1/2	1	1	0	1/2	1/2	1	1/2	-	0	0	1/2	0	0	1	1/2
Anaerobic Degrad	1	1	1	1	1	1	1	1	1	1	1	1	-	0	1	0	0	1	1/2
Insect/Enzyme	1	1	1	1	1	1	1	1	1	1	1	1	1	-	1	1/2	1/2	1	1
Sticky Filter	0	0	0	0	0	0	0	0	0	1/2	0	1/2	0	0	-	0	0	1/2	0
Microwave	1	1	1	1	1	1	1	1	1	1	1	1	1	1/2	1	-	1/2	1	1
Plasma	1	1	1	1	1	1	1	1	1	1	1	1	1	1/2	1	1/2	-	1	1
Hydrogen.	0	0	1/2	1	1/2	1/2	0	0	1/2	1	1/2	0	0	0	1/2	0	0	-	0
Laser pyrolysis	1	1/2	1	1	1/2	1/2	0	1	1	1	1	1/2	1/2	0	1	0	0	1	-
TOTAL	11	7 1/2	10	10 1/2	14 1/2	15 1/2	4 1/2	8 1/2	9 1/2	16 1/2	10 1/2	10	3 1/2	1	16 1/2	1	1	13	6 1/2
NORMALIZED	67	46	61	64	88	94	27	52	58	100	64	61	21	6	100	6	6	79	39

USE FOR TOLERANCE CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	0	0	½	0	0	0	0	0	0	0	0	0	0	½	0	0	0	1
Cross-linking	1	-	1	1	1	1	0	0	0	1	1	0	0	0	1	½	½	1	1
Dissolved Air Flot.	1	0	-	0	1	1	0	½	½	1	1	0	0	0	1	0	0	½	1
Ion Adjust	½	0	1	-	0	0	0	½	½	1	1	0	0	0	1	0	0	0	1
UV/Ozone	1	0	0	1	-	1	0	0	0	1	1	0	0	0	½	0	0	0	1
UV/Ozone/Sonics	1	0	0	1	0	-	0	0	0	1	1	0	0	0	½	0	0	0	1
Electro dialysis	1	1	1	1	1	1	-	1	1	1	1	½	½	0	1	0	0	1	1
Electro osmosis	1	1	½	½	1	1	0	-	½	1	1	0	0	0	½	0	0	0	1
Electro coag	1	1	½	½	1	1	0	½	-	1	1	0	0	0	½	0	0	0	1
Ultra filtration	1	0	0	0	0	0	0	0	0	-	½	0	0	0	1	0	0	0	½
Micro filtration	1	0	0	0	0	0	0	0	0	½	-	0	0	0	1	0	0	0	½
Aerobic Degrad	1	1	1	1	1	1	½	1	1	1	1	-	0	0	1	1	1	½	1
Anaerobic Degrad	1	1	1	1	1	1	½	1	1	1	1	1	-	½	1	1	1	½	1
Insect/Enzyme	1	1	1	1	1	1	1	1	1	1	1	1	½	-	1	1	1	1	1
Sticky Filter	½	0	0	0	½	½	0	½	½	0	0	0	0	0	-	½	½	0	1
Microwave	1	½	1	1	1	1	1	1	1	1	1	0	0	0	½	-	½	0	1
Plasma	1	½	1	1	1	1	1	1	1	1	1	0	0	0	½	½	-	0	1
Hydrogen.	1	0	½	1	1	1	0	1	1	1	1	½	½	0	1	1	1	-	1
Laser pyrolysis	0	0	0	0	0	0	0	0	0	½	½	0	0	0	0	0	0	0	-
TOTAL	16	7	9½	11½	11½	12½	4	9	9	15	15	5	1½	½	13½	5½	5½	4½	17
NORMALIZED	94	41	56	68	68	74	24	53	53	88	88	29	9	3	79	32	32	26	100

USE FOR CAPITAL INTENSITY CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	1	1	1	0	0	1	1	1	0	0	1	1	1	1	0	0	0	1
Cross-linking	0	-	0	½	0	0	0	0	0	0	0	0	½	½	0	0	0	0	0
Dissolved Air Flot.	0	1	-	1	0	0	0	1	1	0	0	0	1	1	1	0	0	0	1
Ion Adjust	0	½	0	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
UV/Ozone	1	1	1	1	-	0	1	1	1	1	1	1	1	1	1	0	0	0	1
UV/Ozone/Sonics	1	1	1	1	1	-	1	1	1	1	1	1	1	1	1	0	0	0	1
Electro dialysis	0	1	1	1	0	0	-	1	1	½	½	1	1	1	1	0	0	0	0
Electro osmosis	0	1	0	1	0	0	0	-	0	0	0	1	1	1	1	0	0	0	0
Electro coag	0	1	0	1	0	0	0	1	-	0	0	1	1	1	1	0	0	0	0
Ultra filtration	1	1	1	1	0	0	½	1	1	-	½	½	½	1	1	0	0	0	1
Micro filtration	1	1	1	1	0	0	½	1	1	½	-	½	½	1	1	0	0	0	1
Aerobic Degrad	0	1	1	1	0	0	0	0	0	½	½	-	½	½	0	0	0	0	1
Anaerobic Degrad	0	½	0	1	0	0	0	0	0	½	½	½	-	½	0	0	0	0	1
Insect/Enzyme	0	½	0	1	0	0	0	0	0	0	0	½	½	-	0	0	0	0	1
Sticky Filter	0	1	0	1	0	0	0	0	0	0	0	1	1	1	-	0	0	0	0
Microwave	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-	0	1	1
Plasma	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-	1	1
Hydrogen.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	-	½
Laser pyrolysis	0	1	0	1	0	0	1	1	1	0	0	0	0	0	1	0	0	½	-
TOTAL	7	16½	10	17½	4	3	8	12	11	7	7	12	13½	15	13	1	0	2½	11½
NORMALIZED	40	94	57	100	23	17	46	69	63	40	40	69	77	86	74	6	0	14	66

USE FOR OPERATING COST CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	1	1	1	1	1	½	½	½	1	1	1	1	1	1	0	0	0	0
Cross-linking	0	-	½	½	0	0	0	½	½	1	1	1	1	1	½	0	0	0	0
Dissolved Air Flot.	0	½	-	1	0	0	0	½	½	1	1	1	1	1	1	0	0	0	0
Ion Adjust	0	½	0	-	0	0	0	0	0	0	0	1	1	1	1	0	0	0	0
UV/Ozone	0	1	1	1	-	½	1	1	1	1	1	1	1	1	1	½	½	½	½
UV/Ozone/Sonics	0	1	1	1	½	-	1	1	1	1	1	1	1	1	1	½	½	½	½
Electro dialysis	½	1	1	1	0	0	-	1	1	½	½	1	1	1	1	0	0	0	0
Electro osmosis	½	½	½	1	0	0	0	-	0	½	½	1	1	1	1	0	0	0	0
Electro coag	½	½	½	1	0	0	0	1	-	0	0	1	1	1	1	0	0	0	0
Ultra filtration	0	0	0	1	0	0	½	½	1	-	½	1	1	1	1	0	0	0	0
Micro filtration	0	0	0	1	0	0	½	½	1	½	-	1	1	1	1	0	0	0	0
Aerobic Degrad	0	0	0	0	0	0	0	0	0	0	0	-	½	½	0	0	0	0	0
Anaerobic Degrad	0	0	0	0	0	0	0	0	0	0	0	½	-	½	0	0	0	0	0
Insect/Enzyme	0	0	0	0	0	0	0	0	0	0	0	½	½	-	0	0	0	0	0
Sticky Filter	0	½	0	0	0	0	0	0	0	0	0	1	1	1	-	0	0	0	0
Microwave	1	1	1	1	½	½	1	1	1	1	1	1	1	1	1	-	½	1	1
Plasma	1	1	1	1	½	½	1	1	1	1	1	1	1	1	1	½	-	1	1
Hydrogen.	1	1	1	1	½	½	1	1	1	1	1	1	1	1	1	0	0	-	1
Laser pyrolysis	1	1	1	1	½	½	1	1	1	1	1	1	1	1	1	0	0	0	-
TOTAL	5½	10½	9½	13½	3½	3½	7½	10½	10½	10½	10½	17	17	17	14½	1½	1½	3	4
NORMALIZED	32	62	56	79	21	21	44	62	62	62	62	100	100	100	85	9	9	18	24

USE FOR SECONDARY WASTE CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	1/2	1/2	1/2	1	1	1/2	1/2	1/2	1/2	1/2	0	0	0	0	1	1	1	1
Cross-linking	1/2	-	1/2	1/2	1	1	1/2	1/2	1/2	1/2	1/2	0	0	0	1/2	1	1	1	1
Dissolved Air Flot.	1/2	1/2	-	1/2	1	1	1/2	1/2	1/2	1/2	1/2	0	0	0	1/2	1	1	1	1
Ion Adjust	1/2	1/2	1/2	-	1	1	1/2	1/2	1/2	1/2	1/2	0	0	0	1/2	1	1	1	1
UV/Ozone	0	0	0	0	-	1/2	0	0	0	0	0	0	0	0	0	1/2	1/2	0	1/2
UV/Ozone/Sonics	0	0	0	0	1/2	-	0	0	0	0	0	0	0	0	0	1/2	1/2	0	1/2
Electro dialysis	1/2	1/2	1/2	1/2	1	1	-	1	1	1	1	0	0	0	1	1	1	1	1
Electro osmosis	1/2	1/2	1/2	1/2	1	1	0	-	1/2	1/2	1/2	0	0	0	1/2	1	1	1	1
Electro coag	1/2	1/2	1/2	1/2	1	1	0	1/2	-	1/2	1/2	0	0	0	1/2	1	1	1	1
Ultra filtration	1/2	1/2	1/2	1/2	1	1	0	1/2	1/2	-	1/2	0	0	0	1/2	1	1	1	1
Micro filtration	1/2	1/2	1/2	1/2	1	1	0	1/2	1/2	1/2	-	0	0	0	1/2	1	1	1	1
Aerobic Degrad	1	1	1	1	1	1	1	1	1	1	1	-	1/2	1/2	1	1	1	1	1
Anaerobic Degrad	1	1	1	1	1	1	1	1	1	1	1	1/2	-	1/2	1	1	1	1	1
Insect/Enzyme	1	1	1	1	1	1	1	1	1	1	1	1/2	1/2	-	1	1	1	1	1
Sticky Filter	1/2	1/2	1/2	1/2	1	1	0	1/2	1/2	1/2	1/2	0	0	0	-	1	1	1	1
Microwave	0	0	0	0	1/2	1/2	0	0	0	0	0	0	0	0	0	-	1/2	0	1/2
Plasma	0	0	0	0	1/2	1/2	0	0	0	0	0	0	0	0	0	1/2	-	0	1/2
Hydrogen.	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	1	1	-	1
Laser pyrolysis	0	0	0	0	1/2	1/2	0	0	0	0	0	0	0	0	0	1/2	1/2	0	-
TOTAL	7 1/2	7 1/2	7 1/2	7 1/2	16	16	5	8	8	8	8	1	1	1	.8	16	16	13	16
NORMALIZED	47	47	47	47	100	100	31	50	50	50	50	3	3	3	50	100	100	81	100

USE FOR PROCESS COMPLEXITY/SIMPLICITY CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	1	0	1	0	0	0	1	1	0	0	0	0	0	0	1	0	0	1
Cross-linking	0	-	0	1/2	0	0	0	1	1/2	0	0	0	0	0	0	1	0	0	1
Dissolved Air Flot.	1	1	-	1	1	1	0	1	1	1/2	1/2	0	0	0	1	1	0	0	1
Ion Adjust	0	1/2	0	-	0	0	0	1	1/2	0	0	0	0	0	0	1	0	0	1
UV/Ozone	1	1	0	1	-	0	0	1	1/2	0	0	0	0	0	0	1	0	0	1
UV/Ozone/Sonics	1	1	0	1	1	-	0	1	1	0	0	0	0	0	0	1	0	0	1
Electro dialysis	1	1	1	1	1	1	-	1	1	1	1	1/2	0	1	1	1	0	0	1
Electro osmosis	0	0	0	0	0	0	0	-	0	0	0	0	0	0	0	1	0	0	1
Electro coag	0	1/2	0	1/2	1/2	0	0	1	-	0	0	0	0	0	1	1	0	0	1
Ultra filtration	1	1	1/2	1	1	1	0	1	1	-	1/2	0	0	0	1	1	0	0	1
Micro filtration	1	1	1/2	1	1	1	0	1	1	1/2	-	0	0	0	1	1	0	0	1
Aerobic Degrad	1	1	1	1	1	1	1/2	1	1	1	1	-	1/2	0	1	1	0	0	1
Anaerobic Degrad	1	1	1	1	1	1	1	1	1	1	1	1/2	-	0	1	1	0	0	1
Insect/Enzyme	1	1	1	1	1	1	0	1	1	1	1	1	1	-	1	1	0	0	1
Sticky Filter	1	1	0	1	1	1	0	1	0	0	0	0	0	0	-	1	0	0	1
Microwave	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-	0	0	1
Plasma	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-	1	1
Hydrogen.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	-	1
Laser pyrolysis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-
TOTAL	12	14 1/2	7	14	11 1/2	10	3 1/2	16	12 1/2	7	7	4	3 1/2	3	10	17	0	1	18
WOMAT 72ED	67	81	30	78	61	56	18	89	60	30	30	22	19	17	56	94	0	6	100

USE FOR MATURITY OF TECHNOLOGY CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	0	½	0	0	0	0	0	0	½	0	0	0	0	0	0	0	0	0
Cross-linking	1	-	1	1	1	1	1	1	1	1	1	½	½	½	1	½	½	1	½
Dissolved Air Flot.	½	0	-	0	0	0	0	0	0	½	0	0	0	0	0	0	0	0	0
Ion Adjust	1	0	1	-	1	1	1	½	1	1	1	½	½	0	1	0	0	0	0
UV/Ozone	1	0	1	0	-	0	0	0	0	1	½	0	0	0	0	0	0	0	0
UV/Ozone/Sonics	1	0	1	0	1	-	1	1	1	1	1	0	0	0	½	0	0	0	0
Electro dialysis	1	0	1	0	1	0	-	½	½	1	1	0	0	0	0	0	0	0	0
Electro osmosis	1	0	1	½	1	0	½	-	0	1	½	0	0	0	0	0	0	0	0
Electro coag	1	0	1	0	1	0	½	1	-	1	1	0	0	0	0	0	0	0	0
Ultra filtration	½	0	½	0	0	0	0	0	0	-	0	0	0	0	0	0	0	0	0
Micro filtration	1	0	1	0	½	0	0	½	0	1	-	0	0	0	0	0	0	0	0
Aerobic Degrad	1	½	1	½	1	1	1	1	1	1	1	-	½	0	½	0	0	½	½
Anaerobic Degrad	1	½	1	½	1	1	1	1	1	1	1	½	-	0	½	0	0	0	½
Insect/Enzyme	1	½	1	1	1	1	1	1	1	1	1	1	1	-	1	1	1	1	1
Sticky Filter	1	0	1	0	1	½	1	1	1	1	1	½	½	0	-	0	0	0	0
Microwave	1	½	1	1	1	1	1	1	1	1	1	1	1	0	1	-	1	1	1
Plasma	1	½	1	1	1	1	1	1	1	1	1	1	1	0	1	0	-	1	1
Hydrogen.	1	0	1	1	1	1	1	1	1	1	1	½	1	0	1	0	0	-	0
Laser pyrolysis	1	½	1	1	1	1	1	1	1	1	1	½	½	0	1	0	0	1	-
TOTAL	17	3	17	7½	14½	9½	12	12½	11½	17	14	6	6½	½	9½	1½	2½	5½	4½
NORMALIZED	100	18	100	44	85	56	71	74	68	100	82	35	38	3	56	9	15	32	26

USE FOR RECOVERY POTENTIAL CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	0	0	0	0	0	0	0	0	½	½	0	½	0	½	0	0	½	0
Cross-linking	1	-	½	½	½	½	½	1	½	1	1	½	1	0	1	½	½	1	½
Dissolved Air Flot.	1	½	-	½	½	½	½	1	½	1	1	½	1	0	1	½	½	1	½
Ion Adjust	1	½	½	-	½	½	½	1	½	1	1	½	1	0	1	½	½	1	½
UV/Ozone	1	½	½	½	-	½	½	1	½	1	1	½	1	0	1	½	½	1	½
UV/Ozone/Sonics	1	½	½	½	½	-	½	1	½	1	1	½	1	0	1	½	½	1	½
Electro dialysis	1	½	½	½	½	½	-	1	½	1	1	½	1	0	0	½	½	1	½
Electro osmosis	1	0	0	0	0	0	0	-	0	½	½	1	½	0	½	0	0	½	0
Electro coag	1	½	½	½	½	½	½	1	-	1	1	½	1	½	1	½	½	1	½
Ultra filtration	½	0	0	0	0	0	0	½	0	-	½	0	½	0	½	0	0	½	0
Micro filtration	½	½	0	0	0	0	0	½	0	½	-	0	½	0	½	0	0	½	0
Aerobic Degrad	1	½	½	½	½	½	½	1	½	1	1	-	1	½	1	½	½	1	½
Anaerobic Degrad	½	0	0	0	0	0	0	½	0	½	½	0	-	0	1	0	0	½	0
Insect/Enzyme	1	1	1	1	1	1	1	1	½	1	1	½	1	-	1	½	½	1	½
Sticky Filter	½	0	0	0	0	0	0	½	0	½	½	0	0	0	-	0	0	½	0
Microwave	1	½	½	½	½	½	½	1	½	1	1	½	1	½	1	-	½	1	½
Plasma	1	½	½	½	½	½	½	1	½	1	1	½	1	½	1	½	-	1	½
Hydrogen.	½	0	0	0	0	0	0	½	0	½	½	0	½	0	½	0	0	-	0
Laser pyrolysis	1	½	½	½	½	½	½	1	½	1	1	½	1	½	1	½	½	1	-
TOTAL	15½	6½	6	6	6	6	6	14½	5½	15	15	6½	14½	2½	14½	5½	5½	15	5½

USE FOR ENERGY INTENSITY CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	1	0	1	0	0	0	0	0	0	½	½	1	1	1	0	0	0	0
Cross-linking	0	-	0	½	0	0	0	0	0	0	0	0	1	½	0	0	0	0	0
Dissolved Air Flot.	1	1	-	1	0	0	0	0	0	0	0	½	1	1	1	0	0	0	0
Ion Adjust	0	½	0	-	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0
UV/Ozone	1	1	1	1	-	½	1	1	1	1	1	1	1	1	1	0	0	1	0
UV/Ozone/Sonics	1	1	1	1	½	-	1	1	1	1	1	1	1	1	1	0	0	1	0
Electro dialysis	1	1	1	1	0	0	-	½	½	1	1	1	1	1	1	0	0	1	0
Electro osmosis	1	1	1	1	0	0	½	-	½	1	1	1	1	1	1	0	0	1	0
Electro coag	1	1	1	1	0	0	½	½	-	1	1	1	1	1	1	0	0	1	0
Ultra filtration	1	1	1	1	0	0	0	0	0	-	1	1	1	1	1	0	0	0	0
Micro filtration	½	1	1	1	0	0	0	0	0	0	-	1	1	1	1	0	0	0	0
Aerobic Degrad	½	1	½	1	0	0	0	0	0	0	0	-	1	½	0	0	0	0	0
Anaerobic Degrad	0	0	0	0	0	0	0	0	0	0	0	0	-	0	0	0	0	0	0
Insect/Enzyme	0	½	0	0	0	0	0	0	0	0	0	½	1	-	0	0	0	0	0
Sticky Filter	0	1	0	1	0	0	0	0	0	0	0	1	1	1	-	0	0	0	0
Microwave	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-	½	1	1
Plasma	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	½	-	1	1
Hydrogen.	1	1	1	1	0	0	0	0	0	1	1	1	1	1	1	0	0	-	0
Laser pyrolysis	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	1	-
TOTAL	12	16	11½	15½	3½	3½	6	6	6	9	10½	13½	18	16	13	½	½	8	2
NORMALIZED	67	89	64	86	19	19	33	33	33	50	58	75	100	89	72	3	3	44	11

USE FOR LABOR INTENSITY CRITERION ONLY

	Liq/Liq Extraction	Cross-linking	Dissolved Air Flot	Ion Adjust	UV/Ozone	UV/Ozone/Sonics	Electro-dialysis	Electro-osmosis	Electro-coagulation	Ultrafiltration	Microfiltration	Aerobic Degradation	Anaerobic Degrad.	Insect/Enzyme	Sticky Filters	Microwave	Plasma	Hydrogenation	Laser Pyrolysis
Liq/Liq Extraction	-	0	0	0	1	1	0	½	0	0	0	0	0	0	0	1	1	1	1
Cross-linking	1	-	0	½	1	1	0	½	½	0	0	0	0	0	0	1	1	1	1
Dissolved Air Flot.	1	1	-	1	1	1	0	1	½	0	0	0	0	0	½	1	1	1	1
Ion Adjust	1	½	0	-	1	1	0	½	½	0	0	0	0	0	0	1	1	1	1
UV/Ozone	0	0	0	0	-	½	0	0	0	0	0	0	0	0	0	½	½	½	½
UV/Ozone/Sonics	0	0	0	0	½	-	0	0	0	0	0	0	0	0	0	½	½	½	½
Electro dialysis	1	1	1	1	1	1	-	1	1	½	½	1	1	1	1	1	1	1	1
Electro osmosis	½	½	0	½	1	1	0	-	0	0	0	0	0	0	0	1	1	1	1
Electro coag	1	½	½	½	1	1	0	1	-	0	0	0	0	0	0	1	1	1	1
Ultra filtration	1	1	1	1	1	1	½	1	1	-	½	1	1	0	0	1	1	1	1
Micro filtration	1	1	1	1	1	1	½	1	1	½	-	1	1	0	0	1	1	1	1
Aerobic Degrad	1	1	1	1	1	1	0	1	1	0	0	-	½	½	1	1	1	1	1
Anaerobic Degrad	1	1	1	1	1	1	0	1	1	0	0	½	-	½	1	1	1	1	1
Insect/Enzyme	1	1	1	1	1	1	0	1	1	1	1	½	½	-	1	1	1	1	1
Sticky Filter	1	1	½	1	1	1	0	1	1	1	1	0	0	0	-	1	1	1	1
Microwave	0	0	0	0	½	½	0	0	0	0	0	0	0	0	0	-	0	0	½
Plasma	0	0	0	0	½	½	0	0	0	0	0	0	0	0	0	1	-	½	1
Hydrogen.	0	0	0	0	½	½	0	0	0	0	0	0	0	0	0	1	½	-	1
Laser pyrolysis	0	0	0	0	½	½	0	0	0	0	0	0	0	0	0	½	0	0	-
TOTAL	11½	9½	7	9½	15½	15½	1	10½	8½	3	3	4	4	2	4½	16½	14½	14½	16½
NORMALIZED	70	58	42	58	94	94	6	64	52	18	18	24	24	12	27	100	88	88	100

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