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**Drinking Water
Engineering and Science
Discussions**

**Interactive comment on
“Optimized conditions for application of organic
floculant aids in water purification”
by P. Polasek**

Anonymous Referee #2

Received and published: 13 January 2010

RESPONSE TO COMMENTS BY THE REFEREE No. 2

Compiled: February 7, 2010

Text in black is the Referee's No. 2 comments
Text in blue is my response

Review of the paper by this Referee is very thorough and to the point and I wish to express my sincere gratitude to him for his input.

I do not find this paper readily understandable, which I attribute to the overall structure, style and a lack of convergence on the concept of optimised conditions as expressed by the paper's title. Too many redundant aspects are incorporated which result in a somewhat fragmented approach. Conversely, certain relevant information is omitted. The fundamental message appears to be that organic flocculant aids increase the settling rate if added at (the author's) $\gamma = 1$, or optimum GT using "high rate clarification technology". In the abstract, the only reference to "optimized conditions" refers to the aforementioned γ (or "measure of flocculation") developed in previous work by the author.

The whole paper deals with the optimized conditions for OFA application which eliminates all problems with respect to the quality of purified water experienced in the engineering practice and facilitates formation of largest and fastest settleable agglomerates.

It is pity the Referee did not consider it appropriate to state at least some of the aspects he considers redundant as well as those relevant information omitted. May be the Editor should given him my second paper where hopefully some of the omitted information could be found.

The inclusion of extensive narrative relating to such earlier work should be reduced through reference. As per Referee #1's point 6: This problem stems from the use of capitalised and abbreviated terminology (POA, IHDS, HRC) rather than simple and concise descriptions. This practice elevates the terminology to an unwarranted status which solicits further definition and extensive explanation.

I believe there is value in the work performed, but this cannot be easily ascertained

given the content and style of the paper in its current form. I recommend that the paper be revised and that sufficient results be included to underpin the conclusions.

The abbreviated terminology of IHDS will be replaced with full description. Since organic flocculant aid and the post-orthokinetic agglomeration method of organic flocculant aid methods of application is frequently referred to I am of the opinion that it is in the interests of easier readability as well as length of the paper to retain to abbreviation of OFA and POA.

Specific Comments:

1. Abstract P206.5: Refers to “aggregation – CPE”, yet the only results presented in the paper relate to the use of inorganic metal coagulants.

The Abstract is adjusted. I can introduce Figures with the results from the use of organic coagulants but the information in these Figures will be very much the same as that in the Figures included in the paper. The only difference will be in the absolute values of the time required to reach flocculation optimum for different organic coagulants and in the description of Figures. It will show nothing new to that already contained in Figures included but this will result in unjustifiably increased extent of paper. Should the Editor insist on including some more Figures I will comply.

2. P206.18: Table 1 adds bulk but little value and should be removed.

The reason why Table 1 is included is to assist the reader in distinguishing between different types of organic polymers used in water treatment and the type of the polymers which corresponds to organic flocculant aid (OFA) that the paper is dealing with. As can be seen from the comments of the Referee No. 1 he is very much confused about the various types of flocculants and purpose of their use. Therefore, in my opinion, Table 1 is very useful. However, if it is considered superfluous there is no reason why it cannot be deleted but I would prefer to keep it there.

3. Introduction P206.25 to P207.9: This section should be revised as it appears almost contradictory when read in the manner presented (i.e. “reduced quantity of floc carryover / lower total residual turbidity: : : and : : : higher residual turbidity produced by the non-separable particles”).

With all due respect I fail to understand what appears contradictory. The reduced quantity of flocs results in lower turbidity. On the other hand, the hydrophilic properties of OFA when it is added under the current method of their application, i.e. together with or shortly after addition of destabilization reagent or organic coagulant, do not allow quantitative reduction of colloidal particles which remain in the purified water as the non-separable particles. It is the content of the non-separable particles which determines the quality of the purified water.

Nonetheless, the section P206.25 to P207.10 was reworded as follows:

It is a common knowledge that the application of OFA often results in a poorer quality of purified water than that obtained without it as well as poorer inefficiency of filter backwashing. Under the common practice, OFA is applied either together with a destabilization reagent (or organic coagulant), or shortly thereafter into a system undergoing aggregation. It is also well known among waterworks operators that OFA applied under such conditions results in the formation of larger flocs of improved settleability thus reducing quantity of floc carry-over from the clarifiers/ sedimentation tanks. This is evident by lower total residual turbidity than that attainable without OFA. On the other hand however, the attained resultant quality of the purified water is often poorer than that to which it is purifiable without OFA. The reason is that a greater quantity of non-destabilized or restabilized particles of impurities than that attainable without OFA remains in the purified water. This is evident by a higher attainable residual turbidity which is produced

by the non-separable (colloidal) particles only. This indicates existence of certain interaction between the aggregating particles of impurities and the OFA.

4. P208.10 and P208.17 (Sections 2 and 3): There is no need to provide an elementary description of organic flocculant aids, which almost implies they are uniquely different from organic polymers in general. Of more benefit would be a well defined characterisation of the polyacrylamides used (in terms of molecular weight distribution, charge density, etc). See the paper of Zhu et al (point 8 below), which illustrates the relevance of molecular weight and charge in such trials. Also refer Yoon et al (Yoon, S.Y., Deng, Y.L., (2004) Flocculation and reflocculation of clay suspension by different polymer systems under turbulent conditions. J. Colloid Interface Sci. 278, 139–145).

The OFA are not uniquely different, they only represent organic flocculants of a certain unique characteristic in comparison to other organic flocculants.

Both papers mentioned are irrelevant to my paper. The paper by Yoon deals with application of cationic polymers, i.e. organic coagulants and therefore has nothing in common with my paper. The paper by Zhe Zhu compares efficiency of cationic and anionic polymers - applied under conditions that most probably they consider to be optimum. In my opinion, in this paper a lot of basic information is missing but the important information with respect to my paper is that they applied anionic polymer shortly after metal coagulant, a method considered in my paper to be far from optimal. Furthermore, by referring to optimal polymer dosage negative influence of OFA on the quality (turbidity) of purified water is indirectly admitted. Regarding characterization of polymers as per paper by Zhu et al. that I am referred to, I must say there is not much to go on. Molecular weight is only referred to as Medium and Ultra high but no definition of what medium and ultra high molecular weight represents, is given. No molecular weight as such is stated. No dosing rates of different polymers the efficiency of which is compared in the paper are stated except it is claimed to be optimal. However, I must admit I learned something new from this paper I was not aware of before, namely that polyacrylamide can also be cationic.

Section 2 will be deleted, Section 3 will remain. The following data will be added:

Molecular weight at pH of typical 0,5% solution at 25 °C of both most efficient Superflocs, namely SFA-110 and SFA-130 is $1.0 - 1.2 \times 10^6$. SFA-110 contains 83% of amide group and 17% of carboxyl group whereas SFA-130 contains 68% of amide group and 32% of carboxyl group (Anonymous, 1970)

5. P209.25: “: : : but the purified water quality is not impaired.” How does this statement equate to the results of Letterman et al and Tambo et al, where deterioration in water quality was observed beyond optimum GT? (Letterman, R.D., Quon, J.E. and Gemmel, R. S. (1973) Influence of rapid-mix parameters on flocculation. J. AWWA, 65(11), 716- 722); (Tambo, N. and François, R. J. (1991) Mixing, breakup, and floc characteristics. In: Mixing in Coagulation and Flocculation (Eds Amirtharajah, A., Clark, M.M. and Trussell, R.R.) AWWA Res. Foundation, Denver Co, 256-281).

My research proved beyond shadow of doubt (Polasek and Mutl, 2005; Polasek, 1972, 1980, 2010 and many others) that both intensity of agitation (high and low) and time its application which is prolonged well beyond the flocculation optimum does not affect purified water quality at all. At a low intensity agitation the quality of purified water may be affected by ineffective enhancement of dispersion and homogenisation of added destabilisation reagent in total volume of water. High intensity agitation produces smaller but denser aggregates and does not impair quality of produced water. However, this topic is not subject of this paper.

6. There is a distinct lack of sufficient results in the paper to validate any major conclusions.

Although at least five primary coagulants are cited, together with three different raw water sources and two polyacrylamides, actual data are not forthcoming and are merely covered by the (approximate) statement “results were very similar” (210.16, P212.14 and P215.27). In lieu of comprehensive results, two “typical” graphs are presented, both of which relate to ferric chloride alone. The passing mention of other primary coagulants used (P210.20 and P211.19-20) and deficit of analytical information seems to defeat the objective of fully understanding the “optimized conditions” implied by the title. Sufficient data concerning the base conditions should be included (raw water, chemicals employed, dosage rates, physical and chemical analyses, etc.). Were no differences observed between the use of metallic and organic polymers as primary coagulants?

This part of the paper is reworded. In my opinion, sufficient data are included on the base conditions. Since I am not trying to prove suitability and efficiency of “primary coagulants” and optimum conditions for their application there is no need to state dosage rate – this may only confuse reader. The tests compared in the individual Figures (pictures) were carried out with the same raw water and the same dosage of “primary coagulants”. The quality of water produced without the use organic flocculant aid is influenced and in fact determined by the reaction conditions applied. The reaction conditions were optimized for the removal of turbidity. This is because turbidity was used as the datum for comparison of the effect of organic flocculant aid on the resultant quality of water and hence to establish the optimized conditions for the application of organic flocculant aid under which no impairment of produced water takes place. There is probably an error in the last sentence because the Referee is referring to metallic and organic polymers as primary coagulants. First of all, the “primary coagulants” used were metal-ion salts of Fe and Al and not metallic polymers. Secondly, the organic flocculant aid does not function as a coagulant aid or perhaps secondary coagulant – the word secondary implies from the primary coagulant. Certainly, there are major differences between the efficiency of metal-ion type “primary coagulants” and organic-polymers coagulants as “primary coagulants”. For instance, SF-577 is not capable of producing sparkling clarity of purified water whereas Floccotan from a certain dosage increases organic pollution of the purified water above that of raw water. However, this is not subject of this paper. I have to refer this Referee, as I referred the referee No. 1 to a paper by Polasek & Mutl (2003): Cationic polymers in water treatment - Part 1: Treatability of water with cationic polymers. *J.WATER SA*, 28, 1, 69-82, 2002; and Part 2: Filtration of water treated by cationic polymers. *J.WATER SA*, 28, 1, 83-88, 2002;

The last sentence has no relevance to my paper at all because it is not dealing with optimization of conditions for the use of any type of “primary coagulant”. If the intention of this last sentence however was to refer to possible differences between agglomeration effect of the aggregates formed by means of metal-ion destabilization reagent and organic coagulant than no differences were observed except for the dosage of OFA which in the case organic coagulants formed aggregates was lower than that for required for metal-ion destabilisation reagent formed aggregates to produce agglomerates of the same sedimentation velocity.

7. P210.16 “: : results obtained were very similar irrespective of water source.” This rather bold statement requires actual values for substantiation. If the results obtained were indeed significantly comparable, then surely this would be worthy of further elucidation, i.e. the notion that application of the (specific) organic flocculant aid is largely independent of the water source and (from point 6 above) the primary coagulation chemicals used. The results obtained with different destabilisation reagents and organic coagulants are significantly comparable and largely independent of the water sources and the destabilisation reagent (organic coagulant) used.

The fluctuation in the raw water quality affects only the optimized reaction conditions under which the aggregation process by means of “primary coagulant” takes place but not the optimized conditions for OFA application.

The quoted sentence will be deleted as it does not belong to Methods and will be moved to Results and discussion where it will be extended and one additional Figure added.

8. Hypotheses appear to be drawn from an investigation in which a multitude of variables are present (see previous points, together with the additional full-scale data, sludge recirculation, etc.). It is not clear how these variables are accounted for in the results, discussion and subsequent deductions. Several are noteworthy, for example data from Table 2 shows that the initial turbidity may have ostensibly varied from 30 to 690 NTU, temperature from 12 to 25_C, etc. As an example of descriptive methodology and inclusion of base conditions, which would allow other researchers to duplicate such experiments, refer to the following paper of Zhu et al where these aspects are clearly presented and the initial variables minimized (Zhu, Z., Li, T., Lu, J., Wang, D. and Yao, C. (2009) Characterization of kaolin flocs formed by polyacrylamide as flocculation aids. Int. J. Miner. Process. 91, 94–99).

In my opinion, it clearly transpires from the results in Figures 1-6 (incl. additional Fig. 3) the only variables affecting the outcome of OFA application are the gamma-value at which PFA is added to the aggregating system and its dosage. The sludge recirculation is undesirable because the OFA conditioned sludge behaves like OFA itself.

The POA method of OFA application was used for dewatering of aluminium sulphate formed sludge discharged from Pulsator type clarifiers. In fact, because this was sludge from a highly eutrophic water the use of OFA under POA method was the only way how effectively to do it – water recovery was about 82%, OFA dosage 0.5 mg/l and SS in the recovered water less 4 mg/l. A new additional Figure is added to show this application. Another application was water from gold mine where content of suspended solids varied between 680 and 20000 mg.l⁻¹.

9. P210.22: No mention is made of when the anionic or neutral forms of polyacrylamide were used, unless the reader is expected to look up the supplier codes (refer point 4).

I don't understand this comment.

Generally speaking, jar tests should be carried out to determine the most suitable OFA for the particular application. My tests proved that in common water purification that SF-A110 and SF-130 are the most efficient OFA. Furthermore, the efficiency of any OFA is very much influenced by the conditions of their dissolution. This topic is dealt with in the second paper that was already submitted to DWES.

An additional Figure is will be included to show the effect of OFA application under POA method for dewatering of clarifier sludge.

10. P210.1 and P211.15 (Sections 5 and 6): Would it not be more appropriate to incorporate the “Jar Tests” section into the “Methods” section?

Both sections will be combined into Methods as suggested.

11. P211.6: “usually” should be qualified.

The word *usually* will be deleted.

12. P211.18: “verified in full scale plants”. Is supporting information available to substantiate this statement, or is this the data provided in Table 3? If so, would the use of an organic flocculant aid in the Clariflocculator (gamma = 0.56) not complement the jar tests (i.e. support the results by highlighting diminished effect at gamma < 1 at full scale)?

The sentence on P211, 16 to 18: The effect of intensity and duration of agitation on the development and properties of aggregates formed was investigated by jar test studies carried out in beakers and the results obtained were subsequently verified in a full size plant. Yes, organic flocculant aid would be added to a system with $\gamma = 0,56$ will complement the jar tests. Regrettably this could not be done because the necessary facility for dosing of OFA did not exist at the waterworks. The effect of $\gamma < 1.0$ on the attained and attainable purified water quality, shown by residual turbidity, is evident from new Figure 3.

13. P211.21-22: “: : changes in the content of anion of added coagulant”. It is unclear as to what exactly is being quantified. Do the anions of the primary coagulants and cations of the flocculant refer to the counterions, i.e. chloride and sulphate and presumably sodium for the polyacrylamide? If the metal itself was the analyte (Fe, Al), then how was polymeric coagulant (CPE) carryover determined? More details regarding the photo-colorimetric method should also be provided.

I am sorry, there is a typing error. The *anion* ... should read *cation* The sentence on P211, 21 to 24 is reworded as follows: *The effect of conditions of agitation on the properties of aggregates formed and their settleability was evaluated by changes in the content of cation of added destabilization reagent (Me) and turbidity (Tu) - total turbidity is designated by quantity C or C₀ (raw water) and affix F thereto means that all separable particles were removed and only non-separable particles remain in the analysed sample. Turbidity was mea-*

14. Comment: P211.26: The results would be strengthened by the inclusion of pertinent analyses such as zeta potential measurements and particle size distributions, rather than relying on tests of aggregation alone (for both jar tests and full-scale evaluation).

Unfortunately, I cannot provide data from zeta potential measurement because this facility was not available. Even if this facility would be available zeta potential would not be able to provide the information about the aggregate (flocs) size-fraction distribution as the test of aggregation does. In contrast to zeta potential measurement, the aggregate (flocs) size-fraction distribution determined by the test of aggregation costs very little as it can be done with basic laboratory glassware and centrifuge. In addition, this is a practical way affordable to any waterworks where sophisticated scientific instruments are not readily available.

15. (a) P212.15: “: : only the results based on turbidity measurements are included: : :”. It would appear that no results are included apart from those provided in Figures 1 and Both of these relate to the use of ferric chloride over a single run, so why include aluminium sulphate and various CPE in the methods?

It is explained in Results and Discussion why the results from turbidity measurement only are shown. Results and Discussion is broadened to include it.

(b) P212.18: “typical results”. Why is only one graph presented in terms of all the jar tests performed and what makes this any different from drawing conclusions based on a single data set?

“Typical results” are not based on a single data set. Figures showing the results obtained from agglomeration of the aggregates formed with other destabilization reagents or organic coagulants will show the same pattern and in principle will differ in the title of such Figure and reference to destabilization reagent or organic coagulant used. Should the Editor insist on more Figures showing the same I will provide it.

16. P214.14-15: “GT > flocculation optimum: : : OFA has no effect”. Are there results to substantiate this statement?

Yes there are results to substantiate it. A new Figure (3) is introduced showing dependence of the attained and attainable turbidity on the gamma value.

17. Comment: The discussion from P214.16 to P215.11 is based on findings from previous work pertaining to the merits of high rate clarification technology. These findings transpire from the results in Figure 1

18. P216.10: The sludge recirculation section almost seems to be an afterthought and requires more comprehensive investigation. The conclusion that recirculation of organic flocculant treated sludge is undesirable is based on four jar tests using only a lime and activated silica process. Why were other chemicals not tested in this manner, considering that lime is rather dissimilar to the previously mentioned primary coagulants? Would ferric chloride, aluminium sulphate or CPE sludge not produce different results? As such, the inference that organic flocculant treated sludge is not desirable can only be made in terms of lime and activated silica, under the conditions and restrictions described.

It is not an afterthought. The effect of recirculation of sludge conditioned with OFA was thoroughly investigated using different destabilisation reagents, organic coagulants as well as decarbonisation with cold lime precipitation reactions. The reason why the OFA on decarbonisation process is shown is: It compares the effect of mineral coagulation (flocculation) aid (activated silica) with OFA. Furthermore, this decarbonisation technology is used by two largest waterworks in South Africa as well as in some power stations.

19. P218.8-10: The word “clarity” appears to be used in two different contexts. What is “actual clarity”? Is one visual and the other measured (if so, how)?

The actual clarity (will be replaced with attainable clarity) means it is produced only by the non-aggregated particles of impurities. It reflects the clarity of purified water which is attainable under the reactions conditions applied to purification process.

20. Table 2: What is the relevance (or value) of including a single THM formation potential?
There is no relevance other than it is another quality parameter of the water used in the tests. It will be deleted from Table 2.

21. Conclusions:

(a) Conclusion 1: Much of the content is discussion and certain parts should be removed in their entirety (e.g. POA definition).

Conclusion 1: It will be reworded as follows: *The optimized conditions for OFA application under which the quality of purified water is not impaired and full agglomeration potential of OFA is fully developed, exist when the aggregation process by means of destabilisation reagent or organic coagulant reaches its flocculation optimum prior to OFA addition. This method of OFA application is called the Post-Orthokinetic Agglomeration (POA) process. Under the POA process, the hydrophilic character of the OFA cannot impair the efficiency of the aggregation process and thereby the purified water quality. The only variables affecting the outcome of OFA application are the gamma-value at which PFA is added to the aggregating system and its dosage.*

(b) Conclusion 2: The statement “: : eliminates all known shortcomings” is not only broad but inappropriate. It does not directly relate to findings presented in the paper.
The word *all* will be deleted.

(c) Conclusion 4: “inexpensive upgrading: : :” cannot be concluded from the paper’s contents. The last sentence of this Conclusion will be modified as follows: *It stands to reason, the HRC process*

(d) Conclusion 5: The body text refers to an upflow velocity of 15.5 m/h (P218.24), whereas the conclusion is based on a reference to previous work (P218.20).

(e) Conclusion 7: This conclusion is not general but rather specific to the lime and activated silica used in the experiment. In addition, the statement “impairment is proportional to OFA dosage” is new.

It is not new, it follows from Figure 3 now Figure 6.

Technical Corrections:

(i) The paper should be revised for minor grammatical errors, e.g. P207.26: “up to the flocculation optimum is reached”; P211.19: “such Floccotan”; P218.9: “eventhough”; Table 2: Consistency in capitalisation (Total Hardness: : : Total alkalinity)
It will be corrected.

(ii) The references are wholly inadequate, which may be rectified by qualifying the “common knowledge” statements and several other assertions, e.g. P207.13
The following additional references will be added:

Anonymous: Private communication with Cyanamid, South Africa (1971)

Mutl S. and Polasek P.: Particle sizes and particle size-fraction distribution in water treatment. *Proc. Conf. IWA, Poster Paper, Melbourne, Australia, April, 2002 (2002)*;

Polasek P. and Van Duuren F.A.: The performance results from the operation of High Rate clarifiers at Bethlehem Municipal waterworks. *Proc. Int. Water Industry '81, Conf. Brighton, UK, June, 1981 (1981)*;

(iii) P208.9: The first figure referenced is Figure 2.
Figures will be renumbered.

(iv) Figure 4: Just an observation, why “right to left”?
The only reason is that in this direction of the OFA dosage increases.

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