STASOFT: A user-friendly interactive computer program for softening and stabilisation of municipal waters

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Abstract

The paper describes the structure of a user-friendly interactive computer program to characterise a water; to determine chemical dosages to soften and/or stabilise the water for municipal use; to evaluate the response of underground waters when pumped to the surface; and to determine the characteristics of blends of two or more waters with different characteristics. The program can be executed only on IBM compatible personal computers and is easy to master.

Introduction

The chemical quality of a water can have a major impact on the system storing and conveying the water, and in the use of the water. Waters from underground sources in dolomitic areas, for example, when brought to the surface, in contact with air, may become oversaturated with respect to calcium carbonate ($CaCO_3$) and cause extensive precipitation in storage dams, canals and pipes. Some waters may attack (be aggressive to) cement-like materials and/or be corrosive to ferrous and other metals. Other waters, in municipal use, may be "hard" due to unduly high concentrations of calcium (Ca) and magnesium (Mg) ions giving rise to high soap demand in washing, furring of hot water appliances and deleterious effects on some industrial processes. All these waters will need to be treated to remove or minimise the various adverse effects. The difficulties with any such water are to assess its characteristics and to devise an appropriate treatment to give a non-scaling, non-aggressive, non-corrosive water.

Guidelines on water quality to limit aggression, corrosion and excess scaling in distribution systems have been set out by Loewenthal et al. (1986). To satisfy these guidelines usually will require the addition of chemicals to the water (chemical conditioning). Here a major difficulty lies in characterising the water (characterisation) and calculating the mass concentrations of the chemicals to be added (dosing estimation).

Characterisation and dosing estimation for waters are based on equilibrium chemistry of the calcium-magnesium-carbonate (Ca-Mg-CO_3) system. This is a complex weak acid/base system existing in three phases, namely gaseous, aqueous and solid. Both characterisation and conditioning may require satisfying equilibrium in one, two or three phases (aqueous, aqueous-solid, aqueous-gaseous or aqueous-gaseous-solid).

Characterisation and dosing estimation employing the basic mass and equilibrium equations defining the Ca-Mg-CO_3 system are cumbersome in the extreme. However, research workers have developed ancillary mass parameters (e.g. alkalinity, acidity) that have greatly eased the problems of measurement for characterisation and dosing estimation.

A major advance in problem solving has been the development of graphically aided procedures, to determine the characteristics of the water and the dosing requirements. Using these procedures, solutions have become readily available and practical for field use. The development of the graphically aided procedures and their application to a wide range of conditioning problems have been dealt with in detail by Loewenthal et al. (1986).

Even though graphically aided procedures are relatively simple, their application still demands a fairly comprehensive understanding of the Ca-Mg-CO_3 system. At water treatment plants the characteristics of the raw water are known quite closely and the treatment procedure is codified to some extent; the problem is to obtain the optimal dosing relevant to a particular day or period. Finding such an optimal solution often demands repeated calculations in which quick solution procedures would be most useful. In consulting practice again rapid assessment of alternative treatment procedures may be required. In all these situations even the graphically aided procedures are relatively slow. To assist in this regard, an interactive "user-friendly" computer program "STASOFT" has been written (Loewenthal et al., 1988) that gives answers rapidly as regards the characteristics of a water, its chemical conditioning and dosing requirements. (This program is available on a floppy disc in executable form from the Water Research Commission, PO Box 824, Pretoria 0001, free of charge to South African chemists, engineers and treatment plant operators). STASOFT should be adequate to provide solutions to the majority of problems the water chemist or engineer is likely to encounter in practice. This paper briefly describes the program, its operation and limitations.

Program structure

STASOFT is executable on IBM compatible personal computers. The program is structured to promote user interaction. It first requests information on water source and the allocation of a file name for storing input data and information generated in the program. It then displays a "menu" of tasks (softening, stabilisation, blending, etc.) from which the user selects the task to be performed. On selection of the task the program prompts the user for the required (measured) input parameters relevant to the task e.g. total alkalinity (i.e. H_2CO_3 alkalinity; and alkalinity (Alk), Ca and Mg, pH, total dissolved solids concentrations (TDS) in mg/ℓ (or alternatively the conductivity), and temperature. From this information it calculates, and displays, associated parameters that assist in characterising the water i.e. ionic strength, total acidity (i.e. acidity), Langelier Index (LI) and calcium carbonate precipitation potential ($CaCO_3$-PP). Having characterised the water, depending on the task, options on the chemicals that may be added for conditioning are presented for selection. The program requests the desired effluent quality parameters and any other information relevant to the task. It then calculates the mass concentration of dosing chemicals and the final state of the conditioned water, and displays the results. Depending on the task there are variations in the input, the derived information and the display, the reasons for which will become readily apparent to the user.

All the input data and information generated in a task are

automatically stored in a file on the disc under a given alphanumeric file name. When a task is completed the program always returns to the task menu where an option is provided to print the task information. With usage a large number of tasks can be filed. At any time, via the "print" option in the task menu, any of these files can be recalled and printed; after printing the selected file the program returns to the task menu. When the program is exited via the "Quit" option in the task menu, the file names accumulated up to that time are displayed together with the disc file space still available, and an option is presented to delete all the files or to retain them. At present no direct provision is made in the program to delete selected files or to transfer the files to another storage disc. However, this can be done under the DOS operating system by an experienced computer user.

Task menu

The task menu contains the following options:

(1) Ca and Mg softening and restabilisation
(2) Evaluation of underground or treated waters when achieving 2 or 3 phase equilibrium
(3) Stabilisation of soft low alkalinity waters; Alk and/or Ca less than about 20 mg/ℓ as $CaCO_3$ ("transition" and "calcium and carbonate species deficient" waters)
(4) Stabilisation of water with Alk and Ca both greater than about 20 mg/ℓ as $CaCO_3$ ("normal" waters)
(5) Blending of two or more waters
(6) Printing a record file
(7) Exiting the program.

The last two options (6) and (7) are not chemical conditioning tasks but ones in connection with the running of the program and have been discussed in the previous section. Tasks (1) to (5) are discussed below.

Softening (Task 1)

Softening involves removal of Ca and Mg, or Ca ions only from the water.

In softening a number of options are presented depending on the raw water and the required softened state. The options are:

Calcium and magnesium removal (high pH softening) using

● Lime [$Ca(OH)_2$] only;
● Caustic soda [$NaOH$] only;
● Lime and soda ash [Na_2CO_3]; and
● Caustic soda and soda ash

Once high pH softening is completed the user can request stabilisation to any selected calcium carbonate precipitation potential ($CaCO_3$-PP) (see *Stabilisation* task below) using carbon dioxide (CO_2). When the task is completed the program returns to the task menu.

Calcium removal only (low pH softening) using

● Soda ash (Na_2CO_3) only;
● Lime [$Ca(OH)_2$] only; and
● Caustic soda [$NaOH$] only

Once low pH softening is completed, yielding a water just saturated (i.e. $CaCO_3$-PP = 0 mg/ℓ), the program returns to the task menu.

Stabilisation (Tasks 3 and 4)

Stabilisation involves conditioning a water so that it will provide a measure of corrosion protection by passivating corrosive surfaces of ferrous materials, not cause aggression to cement-like material and not cause undue scaling. Loewenthal *et al.* (1986) suggest the following guidelines for stability:

(i) Ca and Alk preferably both greater than 50 mg/ℓ as $CaCO_3$ but never less than 30 mg/ℓ as $CaCO_3$;
(ii) Calcium carbonate precipitation potential ($CaCO_3$-PP) between 2 and 5 mg/ℓ $CaCO_3$;
(iii) pH between 7,0 and 9,5;
(iv) Each of the sulphate and chloride ion concentrations not to exceed 50 mg/ℓ in systems with ferrous pipes;
(v) Sulphate ion concentration not to exceed 350 mg $SO_4^=$ /ℓ in systems with normal Portland cement concrete and asbestos cement material; and
(vi) Dissolved oxygen not less than 4 mg/ℓ.

The bases from which these guidelines have been developed are discussed in detail in the monograph by Loewenthal *et al.* (1986) and will not be considered further. However, it should be noted that the Langelier Index (LI) is not included in the guidelines; it is replaced by the calcium carbonate precipitation potential ($CaCO_3$-PP). A positive potential gives the quantitative mass concentration of $CaCO_3$ that can, with time, precipitate out in the water or on the pipe walls, to saturated chemical equilibrium with regard to the solid $CaCO_3$; a negative value gives the dissolving potential. In contrast the Langelier Index is only a qualitative measure of tendency to precipitate or dissolve $CaCO_3$ — for the same LI two waters may have $CaCO_3$-PP values that differ widely. In the solution, both the LI and $CaCO_3$-PP of the treated water are displayed even though the use of the LI is not recommended. This is done for two purposes, to highlight the inconsistency of the LI in quantifying the state of over and under-saturation when compared to the precipitation potential, and to serve as a bridge to the user converting from the Langelier Index to the precipitation potential.

For stabilisation, waters are essentially classified into two categories designated "normal" and "calcium and carbonate species deficient" waters, respectively.

A "normal" water is one in which both the Ca and Alk guidelines can be satisfied and the $CaCO_3$-PP guideline can be attained within the pH range of 7 to 9,5, by the addition of *one* chemical only as follows; if the water is undersaturated, by the addition of either lime, caustic soda or soda ash; if the water is oversaturated (which is uncommon) by the addition of either a strong acid or CO_2. Usually a water with Ca and Alk both > 20 to 30 mg/ℓ as $CaCO_3$ will behave as normal water. Many inland waters in South Africa fall into this category.

A "calcium and carbonate species deficient" water is one in which the Ca and/or Alk are so low (both approximately less than 10 mg/ℓ as $CaCO_3$) that it is not possible to achieve a positive $CaCO_3$-PP by the addition of only a strong base (lime or caustic soda). To stabilise such a water to satisfy the stabilisation guidelines, the addition of lime and carbon dioxide is required. Waters derived from Table Mountain sandstone regions in South Africa are typical of this category.

A "transition" water is one intermediate between the waters in the two categories above, a hybrid category, because its treatment involves features from both previous categories. Roughly, if a water has an Alk and/or Ca in the range 10 to 25 mg/ℓ as $CaCO_3$ it may be possible, by the addition of one chemical only,

to obtain the required $CaCO_3$-PP (2 to 5 mg/ℓ) but the Ca and/or Alk may be less than the minimum specified (30 to 50 mg/ℓ as $CaCO_3$ for both), and/or the pH may be greater than 9,5. In order to satisfy the stability guidelines the water must be stabilised by the addition of lime and carbon dioxide, as for a calcium and carbonate species deficient water.

It is sometimes difficult to assess *ab initio* in which category a water falls. This difficulty has been recognised in the program. When in doubt select task (4) in the menu i.e. the task dealing with a normal water. If the water is calcium and carbonate species deficient this is displayed at the characterisation stage and the program cannot proceed further in its stabilisation function — the program instructs the user to select task (3) i.e. the task dealing with "calcium and carbonate species deficient" and "transition" waters; if task (4) provides a solution but the Ca and/or Alk is less than the minimum concentrations specified in the range 30 to 50 mg/ℓ as $CaCO_3$, or the pH is greater than 9,5, the water in fact is in the transition category — the program displays the dosing information and the fact that the water is not adequately stabilised, and instructs the user to repeat the stabilisation calculation, using task (3).

The stabilisation guidelines suggest the absolute minimum concentrations for both Ca and Alk at 30 mg/ℓ as $CaCO_3$. Should the user judge these minimum values too high or too low he/she is free to select other minimum values.

The dosing calculations satisfy the stabilisation guidelines only insofar as these are concerned with the Ca-Mg-CO_3 system. Guideline (iv), relating to the corrosive effect of the sulphate and chloride content of a water to ferrous materials, still needs to be considered. This guideline is an empirical one based on experimental and full-scale behaviour of distribution systems with ferrous components. The guideline serves a cautionary function — qualitatively the higher the $SO_4^=$ and/or Cl^- concentrations the higher the corrosion rate and the shorter the life of ferrous components in the system. The corrosion stimulating effect of $SO_4^=$ and Cl^- is reduced to some degree by the alkalinity in the water but no quantitative data are available to assess this with any degree of reliability (See Loewenthal *et al.* (1986) for a more detailed discussion). With high $SO_4^=$ and Cl^- concentrations consideration should be given to replacing ferrous pipes with cement and plastic ones.

With regard to guideline (v), relating to the aggressive effect of sulphate content of the water, normal cement can be used for water with $SO_4^= < 350$ mg $SO_4^=$ /ℓ; if $SO_4^= > 350$ mg $SO_4^=$ /ℓ, low tricalcium aluminate cement should be used.

Water blending (Task 5)

Two or more waters (up to 9) with different characteristics (Alk, C, Mg, pH, TDS, temperature) are blended in some selected proportions. The program requests the characteristics and blend proportions of each water and calculates the characteristics of the blend. The blend will be either oversaturated, saturated or undersaturated and the user is provided with an option to stabilise the blend to satisfy the stabilisation guidelines.

Underground or treated water in equilibrium with CO_2 partial pressure (Task 2)

Underground and surface treated waters, when exposed to air, will absorb or discharge CO_2 until equilibrium is attained between the CO_2 partial pressure in the air and the concentration of dissolved CO_2 in the liquid. Loss of CO_2 may cause oversaturation in the liquid phase with associated $CaCO_3$ precipitation. Alter-

natively, if the water is sufficiently undersaturated, loss or gain of CO_2 may cause a change in the undersaturated state. An example is underground waters in dolomitic areas; such waters may be in equilibrium with $CaCO_3$ solids at a high underground partial pressure of CO_2; when brought to the surface, CO_2 *loss* may cause massive $CaCO_3$ precipitation. In other situations the water may *absorb* CO_2 from the air and become undersaturated.

The program requests the Alk, Ca, TDS, *in situ* pH, and *in situ* temperature. By *in situ* pH and temperature is meant

● for *treated waters* the pH and temperature immediately after treatment; and

● for *underground waters* the pH and temperature underground.

From this input, it characterises the state of the water. For *treated waters* the characteristics should be the same as those calculated after softening and stabilisation. For *underground waters* the characteristics should be consistent with the environment underground, e.g. underground water from dolomitic areas should have a $CaCO_3$-PP of near zero in its underground state, i.e. it should be in equilibrium with the solid $CaCO_3$ phase at the relatively high underground CO_2 gaseous partial pressure. Once the program has calculated the *in situ* characteristics, it determines the characteristics the water will attain with time at the surface under the partial pressure of CO_2 in the atmosphere (or any selected CO_2 partial pressure) and the surface temperature. If the underground water becomes oversaturated when brought to the surface environment, the mass concentration of $CaCO_3$ that can precipitate to attain 3 phase equilibrium is calculated. Should the water become or remain undersaturated, the program calculates the lime dosage to stabilise the water to a $CaCO_3$-PP of around zero, for transportation in closed conduits.

Program limitations

The program must NOT be used for the following tasks:

● The TDS of the water should not exceed about 1 000 mg/ℓ i.e. not exceed an ionic strength of 0,02. At higher TDS depending on the ionic species present and their concentrations (in particular the cations Mg^{++}, Ca^{++} and Na^+ and the anions $SO_4^=$, $CO_3^=$ and HCO_3^-), ion pairing effects can become increasingly significant. These effects need to be incorporated if accurate characterisation and dosing estimation are to be made, but this requires inputs of the concentrations of the ions listed above plus the concentrations of other species that contribute significantly to the ionic strength, usually Cl^-. This class of water is occasionally encountered with municipal supplies but more commonly with cooling tower and mining operations. A computer program for these waters similar to the one described in this paper, is in preparation.

When the TDS exceed about 10 000 mg/ℓ then, in addition to ion pairing effects, ionic hydration becomes significant. Furthermore, at these high salinities, in pH measurement the residual liquid junction potential causes the pH reading (on a pH meter calibrated against NBS buffers) to deviate appreciably from the true pH. These waters can be characterised and conditioned by means of graphical aids or a special computer program (available from us), but at 25°C only. Characterisation and conditioning of this class of water are discussed in detail by Loewenthal and Marais (1984).

● In water reclamation, for the calculation of lime requirements in the high lime treatment stage of biologically

treated secondary effluents. The presence of organic material increases the apparent $CaCO_3$ solubility product by an order of magnitude. No provision has been made in the program for changes of the solubility product due to the presence of organic material. After carbon filter treatment the solubility product reverts to that for normal water and conditioning problems can be resolved using this program.

In due course the program will be extended to deal with the high lime treatment phase; in the interim for a solution, using graphically aided procedures, the reader is referred to Wiechers (1977) and Wiechers et al. (1980).

● Stabilisation of natural soft brown waters containing humic and fulvic acids. These acids give rise to two effects:

The humic and fulvic acids have acidities and alkalinities additional to those due to the carbonate system. The theoretical relationships in the program relate to those for the carbonate system only. In consequence dosage calculation from inputs of alkalinity and pH, determined on the natural brown waters using the methods developed for the carbonate system, will be in error.

The humic material slows down the rates of both dissolution and precipitation of solid $CaCO_3$; in practical terms these are equivalent to a pseudo (apparent) *high* solubility product for dissolution of $CaCO_3$ (see Loewenthal et al. 1986 for details). Once colour has been removed, the program procedures apply.

Discussion

● In demonstrating the program to new users, the authors found little difficulty in running the program and solving a variety of conditioning problems. Perhaps the most satisfying aspect that emerged was the change in attitude engendered in some users in their recognition of the superiority of the equilibrium chemistry approach over the semi-empirical stoichiometric approach at present in vogue. Users also intimated that, in working with the program with a gradually changing influent water quality, from the observed solutions they developed a "feel" for the way the conditioning responses behave. If these opinions find more general support by practising water chemists, engineers and operators it should lead to improved plant design, plant operation and control, consistently yielding properly stabilised water.

● Although great practical advantages are envisaged with the use of the program a warning relevant to this and other programs simulating physical phenomena is in order: Computer programs simulate the behaviour of physical phenomena within a set of rules that usually do not encompass the totality of the phenomena behaviour; as a consequence computer programs can never substitute for basic understanding of the phenomena, they only facilitate the use of algorithms for solving problems within the structure of knowledge written into them. Users therefore should not omit to study the "source" material available on the $Ca-Mg-CO_3$ system in the monograph by Loewenthal et al. (1986); without a good understanding of the $Ca-Mg-CO_3$ system the chances of misapplying solution procedures are increased.

● The monograph solutions are based on solubility product constants for $CaCO_3$ (with its temperature dependency), K_{sp}, derived by Larson and Buswell (1942), whereas the user manual solutions are based on K_{sp} values derived by Plum-

mer and Busenberg (1982). To allow direct comparison between the monograph and computer solutions an option is provided in the program to select the 1942 constant values. The examples in the user manual have been based on 1942 constant values to allow direct comparison with the graphical solutions in the manual.

◐ The validity of a calculated solution depends on the correctness of the experimentally determined input data. Here again a good understanding of the characteristics of the $Ca-Mg-CO_3$ system will prevent errors. For example, the practice of recording the pH of a sample at the laboratory is almost certain to lead to quite erroneous characterisation of the sample because the pH and acidity will change due to loss or gain of CO_2 during the time interval between sampling and pH measurement. With understanding of the $Ca-Mg-CO_3$ system, the user will know that correct characterisation is possible if the pH is measured *in situ*, in the field, whereas the alkalinity measurement can be delayed to any subsequent convenient time.

● What of the future? The program does not allow for ion pairing or hydration effects. The first effect only becomes significant above a TDS of about 1 000 mg/ℓ and the second above 10 000 mg/ℓ. Incorporation of the effects demands additional experimental input of the concentrations of the principal ionic species (usually Ca^{++}, Mg^{++}, Na^+, $SO_4^=$, $CO_3^=$, Cl^-). As most municipal water sources have TDS < 1 000 mg/ℓ there was no need to provide for these "high salinity" effects. However, in mining waters and cooling tower operation, for example, the TDS limit is likely to be exceeded and the more elaborate analysis incorporating high salinity effects is indicated; programs to deal with these waters, suitable for personal computers, are under development.

Acknowledgement

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