

BREWING LIQUOR—A REVIEW*

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*(Heron & Comrie, Trafford Laboratory, Manchester, 17)**Received 14th December, 1966*

Among the ions present in brewing liquor, calcium is of outstanding importance because of its beneficial effect, in conjunction with phosphate, in lowering the pH in the mash tun; the bicarbonate ion, which acts in the reverse direction, is undesirable. The effect of ions on flavour is not easy to assess but sodium, magnesium, chloride and sulphate are of importance in this connection. Liquor treatment, involving prior removal of ions followed by addition of hardening salts, is discussed in detail in the context of modern plant operation.

No great changes in our knowledge of the subject of brewing liquor and its treatment have taken place during the last ten years, but it is perhaps as well to be reminded from time to time of what is known. It is easy to adopt a routine way of doing something and forget the reasons for it, so that if any unusual circumstance arises one is momentarily at a loss. Most beers contain about 94% of water, and it is therefore not surprising that the nature of the water is important. Not only do the salts it contains in small amounts contribute to the flavour of the beer, they influence the complex enzymic activities of the mash and they help to regulate the changes that occur during boiling, cooling and fermentation of the wort.

REQUIREMENTS OF A BREWING LIQUOR

What is required in a water that is to be used for brewing?

First, it must be wholesome. By that is meant that it conforms to the standards of a drinking water. Since all water used in the actual brewing process is strongly heated, if not boiled, it might be thought that some laxity regarding bacterial contamination might be allowed, but this would be unwise. The same water supply is generally used for washing plant, and may be added in small quantities directly to the beer or yeast. Moreover, the build-up of infection that may occur in pipes or tanks can have a direct effect on the flavour of the wort and therefore of the beer. Once it has been established that the water is wholesome, we are interested in the nature and amount of the salts it contains. These are ionized in solution, and

the best way to talk about them is as ions. The principal ions present are those of calcium, magnesium, sodium, potassium, sulphate, chloride, nitrate and carbonate. A minor ion is silicate, and there may be traces of iron and other heavy metals. As in the case of drinking water, no toxic metal should be present in more than a trace and is, in fact, unlikely to be there at all.

The ionic concentrations can be expressed as p.p.m. or grains per gallon. Since brewers are more familiar with the latter, I shall use that mode of expression. As a close approximation, p.p.m. are 14 times gr./gal.

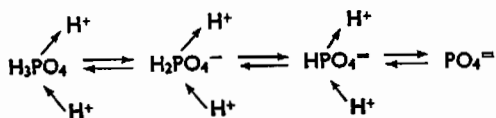
What the brewer wants above all is calcium, then possibly a small amount of magnesium. He does not want nitrate, nor does he want carbonate, except possibly in stouts so, to keep the ionic balance, he has to have sulphate or chloride or a mixture of both. The calcium ion is necessary because it lowers the pH of the mash towards the optimum for enzymic action, it helps to precipitate unwanted nitrogen, and it prevents the over-extraction of nitrogen from the grains and of resin from the hops. It is needed to facilitate fining and yeast flocculation and to prevent the precipitation of oxalate in the beers.

Magnesium is needed for yeast nutrition, and it is probable that there is enough in the malt for this purpose, but a small amount in the water is a safeguard. The alkalis are needed simply in order to introduce the chloride ion for purposes of flavour.

The calcium ion.—It has just been said that calcium lowers the pH of the mash.

* This paper was read to the Scottish Section on 8th November, 1966.

It does so by its interaction with phosphates and protein from the malt. The phosphates form an equilibrium mixture of ions:



the majority being primary ions, H_2PO_4^- . In moving from left to right along this system, H^+ ions are set free in three stages. By forming an insoluble tertiary salt, and a secondary salt which is only slightly soluble, calcium ions remove the PO_4^{3-} and a proportion of the HPO_4^{2-} , so causing a movement to the right to make good the loss. This liberates H^+ ions and lowers the pH of the mash. Magnesium does not have the same effect because secondary and tertiary magnesium phosphates are comparatively soluble, and in fact, when present in quantity, magnesium tends to delay the precipitation of tertiary calcium phosphate until the wort is boiled, so diminishing the fall in pH in the mash tun and increasing it in the copper. Sodium has a somewhat similar action. The ions of calcium and magnesium, being bivalent, will also cause the precipitation of some of the protein of the mash, and this in its turn causes a slight additional fall in the pH.

It was originally believed that the phosphorus concerned in the above reaction was entirely inorganic, but we now know that it is mainly organically combined phosphorus which is involved. This type of compound yields primary potassium phosphate on hydrolysis, and the ionic equilibrium which has been described is probably as good a way as any in which to represent the reactions with calcium, although it may not be literally correct.

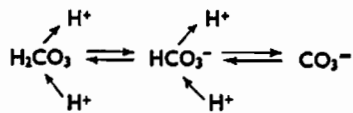
Consider now what effect this fall in pH of the mash is going to have. α -Amylase has a pH optimum at 5.7, β -amylase at 4.7, and the proteolytic enzymes of malt have optima between 4.2 and 5.0. The pH of a malt mashed with pure water is in the neighbourhood of 6.0 so that calcium ions, by lowering the pH, will favour saccharification and proteolysis, leading to increased extract from the malt and a rise in the amount of readily-soluble nitrogen in the wort. Calcium ions, as such, also have a

protective action on α -amylase, and extend the range of optimal pH of all the enzymes. The phosphates are the principal buffering substances in wort, and calcium ions, by precipitating phosphates, cause a reduction in buffering capacity which more than offsets the slight increase in buffering (due to amino acids) which results from the stimulation of proteolysis. As will be seen later, this has a favourable effect on the pH of the beer. Calcium ions also initiate the precipitation of oxalate derived from the malt, which continues to come out of solution as beerstone throughout the brewing process. In the absence of sufficient calcium, oxalate precipitation may be unduly delayed and can in some circumstances cause haze in beer or overfoaming.

The influence of calcium continues into the sparging stage, for here any undue rise in pH will increase the extraction of colouring matter, astringent bitter-flavoured substances and silica from the grains, and will peptize a small amount of nitrogenous matter which is liable to give haze trouble later on. In the copper, the precipitation of insoluble calcium phosphate that was started in the mash tun is completed and the pH of the wort falls slightly. The lower pH produced by calcium ions lessens the rate of extraction of the soft resins of the hop, and slows up the speed of their conversion to the more soluble iso-products. The wort will therefore be less bitter and contain less preservative; indeed, a highly gypseous liquor has been called a hop-waster since, to get the same degree of bitterness, more hops have to be used. This wastage of hop resin may be augmented by the increased flocculation of protein and protein-tannin which takes place at the lower pH, since the flocculum adsorbs hop resin. Apart from this possibility, the improvement in copper break and cold break makes an important contribution to the health of the fermentation and the soundness of the beer. The improvement is due in part to the lower pH, and in part to the actual concentration of calcium and magnesium ions and their precipitating action on protein, as in the mash. The calcium ions also have the property of restraining colour formation during the boil, particularly of the reddish shades that enter into the colour of beer.

The carbonate ion.—Carbonate opposes the good work of calcium in the mash tun,

sparge and copper. We can see why if we look at its ionic equilibrium, which is



and since H_2CO_3 is lost (as CO_2) under the conditions of temperature and acidity of the mash, the equilibrium is displaced from right to left and H^+ ions are absorbed, so raising the pH. Furthermore, roughly twice the number of H^+ ions are removed in moving from CO_3^{2-} to H_2CO_3 as are set free by an equivalent amount of calcium in moving from a mixture of H_2PO_4^- and HPO_4^{2-} to PO_4^{3-} , which means that the carbonate ion is twice as effective in raising the pH as the calcium ion is in lowering it. In actual fact the carbonates in a water generally exist as bicarbonates, and there is only one H^+ ion removed from solution in passing from HCO_3^- (the bicarbonate ion) to H_2CO_3 , but the number of bicarbonate ions is double the number when expressed as carbonate ions (*i.e.*, $\text{Ca}(\text{HCO}_3)_2$ is conventionally expressed as CaCO_3) so the result is the same.

Like the precipitation of tertiary phosphate, the loss of H_2CO_3 as CO_2 is partly delayed until the wort is boiled, when its loss has the effect of diminishing the fall in pH that occurs on boiling. The carbonate ions, by raising the pH, will tend to give less fermentable worts and leave a larger amount of undegraded nitrogenous matter in colloidal solution. They will foster the extraction of undesirable substances from the grains during sparging, produce wort of higher colour and an increased but somewhat harsher bitterness in the copper, and give a less clean separation of unstable protein and protein-tannin compounds. They therefore tend to lower the non-biological stability of the beer and, if present in any significant quantity in make-up liquor added to the hopped wort, they can also lower the resistance of the beer to lactic infection by raising its pH.

Nitrate and silicate.—The nitrate ion serves no useful purpose in brewing liquor, and in amounts of more than about 3 grains per gallon it will cause progressive deterioration of the yeast. The actual poisoning is probably due to nitrite produced by bio-

chemical reduction of the nitrate, and its toxicity is enhanced by the presence of chloride ions in excess of about 20 grains per gallon. Yeasts vary in their susceptibility, but a nitrate content of not more than 2 grains per gallon is generally harmless. The presence of silica in more than small amount, whether derived from the brewing liquor—which is unlikely—or extracted from the grains by sparging at too high a pH, has been known to cause trouble by forming a protein complex which is adsorbed on the surface of the yeast and hampers its activity.

Flavour effects.—Exaggerated claims have sometimes been made regarding the influence of liquor composition on the flavour of the beer, but even when these are discounted there remains the fact that the flavour given by the malt and the hops is influenced to some extent by the presence of certain ions in the liquor which persist into the beer. These ions are those of magnesium, sodium, chloride and sulphate. The magnesium ion has a very marked sour-to-bitter flavour, and can be detected in concentrations of little more than 1 grain per gallon. Sodium has a slightly sour-saline effect on the palate, potassium is purely saline, sulphate is rather more dry and bitter, and the chloride ion is sweet and full. Three things follow from this: (a) the amount of magnesium must be kept low; (b) the sulphate/chloride ratio should be higher in bitter beers than in mild ales; and (c) the balance of flavour from sodium linked with chloride is better than from sodium linked with sulphate. A fourth flavour effect is due to the fact that the chloride ion can be tasted at a concentration lower than the sodium ion, from which it follows that an increasing concentration of sodium chloride will start by being sweet and end by being mawkish and unclean. For this reason some brewers prefer to add potassium chloride in place of sodium chloride, as the potassium ion is free from the slightly sour flavour of the sodium ion. Indirectly, calcium has a beneficial effect on the flavour of the beer as a result of its influence on the pH of the wort, but excess of calcium, by its effect on proteolysis and hop extraction, produces a harsh, thin flavour, lacking in hop character.

Effect of trace elements.—In addition to the ions which have been discussed, there are others which may be found in a water supply in very small amounts which are not without

significance. Iron, and its frequent companion manganese, will upset yeast and give an off-flavour to beer if present in more than a few parts per million, but in solution it is hardly likely to survive the brewing process to any significant extent. As a liquor contaminant, therefore, it is more likely to cause trouble in pipelines than in the brewing process itself. Copper is known to be toxic to yeast if present in wort in excess of about 10 p.p.m., but the amount contributed by any natural water would be insignificant compared with the amount dissolved from the copper plant in the brewhouse. Fluorine in water has assumed dietary importance in recent years, and added (as fluoride) to water supplies in some parts of the country to ensure a concentration of about 1 p.p.m. This concentration has been found to be quite without effect on fermentation and yeast health, and the yeast itself is not harmed by concentrations up to 10 p.p.m.

the quantities of the different salts needing to be added to pure water to get these ions in solution (remembering that the bicarbonates are conventionally expressed as carbonates: it makes no difference to the calculations). The two forms of expression are necessary because, although we may think in terms of ions, we have to add these ions as salts.

A typical analysis is set out in Table I. For the sake of simplicity both the alkali metals (sodium and potassium) have been expressed as sodium.

REMOVAL OF CARBONATE

In most cases the only ion that needs removing from a water to make it suitable for brewing is the carbonate. The removal can be done by boiling, treatment with acid, treatment with lime followed by adjustment of the pH, or by "starvation" ion exchange.

TABLE I
WATER ANALYSIS

Ions			Salts		
	gr./gal.	p.p.m.		gr./gal.	p.p.m.
Na	0.5	7	NaNO ₃	1.40	19.6
Mg	0.5	7	NaCl	0.28	3.9
Ca	5.0	70	MgCl ₂	2.00	28.0
NO ₃	1.0	14	CaCl ₂	2.08	29.1
Cl	3.0	42	CaSO ₄	4.25	59.5
SO ₄	3.0	42	CaCO ₃	7.50	105.0
CO ₃	4.5	63			

As far as fluorine is concerned, therefore, any water which is safe to drink is safe for brewing. Free chlorine in excess of about 0.5 p.p.m. which can sometimes be found for short periods as a result of chlorination of a public supply, can produce an off-flavour in beer, especially in the autumn when the water is liable to contain traces of organic matter.

LIQUOR TREATMENT FOR BREWING

In order to work out any form of liquor treatment, it is first necessary to know what is in the liquor to begin with. This information is contained in an analysis of the liquor, which will probably set out the mineral constituents in two forms: first as the quantities of the ions present, and then as

Boiling.—Boiling can, in favourable circumstances, reduce the content of calcium carbonate to about 4 grains per gallon which is sufficiently small to be harmless, but it will not remove magnesium carbonate to the same extent and has no effect on sodium carbonate. This method is therefore only effective if most of the carbonate is combined with calcium, although the addition of calcium chloride equivalent to the sodium carbonate (0.86 pints of a saturated solution per 100 brl. for each grain per gallon of sodium carbonate) and the magnesium (3.8 pints per 100 brl. for each grain per gallon of magnesium) before boiling will increase the removal of carbonate. With the present cost of fuel the method is expensive.

Treatment with acid.—The acids commonly

used are sulphuric, phosphoric and lactic. Phosphoric and lactic acids produce buffer salts which tend to keep the pH of the beer above its best range, so sulphuric is the acid most favoured unless the water already contains a large amount of sulphate. Acidification may be partly or entirely carried out by means of an acid salt, so avoiding the difficulty of handling a strong acid and lessening the risk of over-acidification. Sulphuric acidification is less suited than other treatments to water containing more than a trace of iron, or one containing much alkali carbonate, and it must be remembered that the CO₂ which is disengaged can be corrosive unless means are used to drive it off.

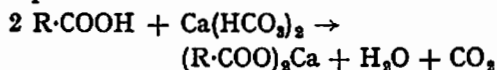
Treatment with lime.—The problem of obtaining removal of carbonate without leaving the liquor alkaline has been tackled in two ways. In one, the carbonate is precipitated with a small excess of lime and allowed to settle for 1–4 hr. The liquor is then passed through a bed of carbonaceous calcium zeolite, which removes the excess lime, and any remaining calcium and magnesium carbonates, down to about 1 grain per gallon, leaving the water with a pH of 6.9–7.1. Other salts of calcium and magnesium are unaffected. In the other process, the carbonates are again precipitated with lime and any excess of lime, together with a fraction of the precipitated calcium carbonate, is neutralized with sodium or potassium bisulphate. The process is simple and it can, if necessary, be carried out in the one hot liquor tank equipped with means for mixing-in the reagents and holding back the precipitated calcium carbonate. It has the advantage of coping with slight variations in raw liquor composition and removing moderate amounts of iron and manganese. If two tanks are available the liquor is transferred to the second one before adding the bisulphate, and whether one or two tanks are used care must be taken that the deposit remains undisturbed when the water is drawn off.

If the demand is sufficient to warrant it, this type of treatment can be carried out continuously and very efficiently in plant designed specifically for the purpose and operating on the "blanket" principle. The raw water and milk of lime or lime water are injected tangentially in the calculated proportions at the base of a tower which becomes wider towards the top. Precipitation of

calcium carbonate takes place rapidly and the particles gradually increase in size, so that by the time the water reaches the upper part of the tower they will have become sufficiently large to fall to the bottom, where they are periodically withdrawn as small beads that rapidly drain free of water. The decarbonated water leaves the top of the tower under slight pressure and may need filtering to become perfectly bright. The pH will also need adjusting with acid or acid salt as in the batch treatment. The operation takes place best at normal well water temperature and can be made automatic.

"Starvation" ion exchange.—In this process the liquor is passed through a weakly acidic carboxylic resin, an ion-exchange material, as a result of which only those cations (Na, K, Ca, Mg) which are combined with a weak acid (CO₃) are replaced by hydrogen ions. The free carbonic acid so formed is removed by passage through a degassing tower, and we are left with a liquor from which all the carbonates (including those of sodium and potassium if present) have been removed, leaving the other salts (chloride, sulphate, nitrate) unaffected.

The exchange and degassing may be shown in equation thus:—



The critical stage of this process is the regeneration of the ion-exchange material, which is done with sulphuric acid in carefully restricted amount. Regeneration must be stopped as soon as the first sign of acidity appears in the effluent, for if full regeneration were allowed to take place cation exchange would not be selective and nothing but free acids would be left in the treated liquor.

The pH of the decarbonated liquor is suitably adjusted by the addition of a small amount of lime water or caustic soda solution before it receives any hardening salts. The process has the advantage of being almost continuous, of coping with variation in water composition, and of being amenable to automatic control.

One final word about decarbonation. It should be applied to *all* the liquor—mashing, sparging and make-up.

It will be remembered that the reason for removing carbonate was in order to reduce the pH of the mash, and that the same effect could be produced by the addition of calcium

ions. Where the carbonate content is moderate and there is no large concentration of other salts, the carbonate, instead of being removed, may be offset by adding calcium salts—mainly sulphate if the liquor is to be used for pale ales and partly chloride if it is required for mild ales. The quantity of calcium needed for this purpose is such that the total calcium in the liquor after the addition is at least twice the equivalent of the carbonate present, and preferably more if some of the carbonate is combined with magnesium (2 grains of calcium are equivalent to 3 grains of carbonate). Where it occurs naturally, as in the well waters of Burton-on-Trent, such a "neutralization" of carbonate by the total calcium present gives good results, but on the whole it is preferable to remove the carbonate, or at least reduce it to about 4 grains per gallon as calcium carbonate.

ADDITION OF SALTS (HARDENING)

The actual amount of any type of salt required in a liquor is largely a matter of opinion, based on the character of the beer that is being brewed. In the days when gravities were commonly 1045–1055, as much as 20 grains per gallon of calcium would be demanded for pale ales, but the amount fell to about half this figure with the diminution in gravities. With a better realization of the importance of adequate flocculation during boiling and cooling, there has been a tendency recently for the amount to rise again, and it now varies between 7–14 grains per gallon for pale ales, 4–8 for mild ales, and 2–4 for stouts, these quantities being additional to what is required to offset unremoved carbonate. In pale ales the larger proportion of this will be as sulphate, but in mild ales it will be in more nearly equal amounts of chloride and

TABLE II
COMPOSITION OF SOME BREWING LIQUORS
(grains per gallon)

Pale ales		Mild ales		Stouts	
Ions	Salts	Ions	Salts	Ions	Salts
Ca 7–14	CaSO ₄ 15·7–31·5	Ca 4–8	CaSO ₄ 5–10	Ca 2–4	CaSO ₄ —
Mg 0·5	CaCl ₂ 6·9–13·7	Mg 0·5	CaCl ₂ 7–14	Mg 0·5	CaCl ₂ 5·5–11
Na 1–2	MgSO ₄ 2·5	Na 2–4	MgSO 2·5	Na 2·8–4·8	MgSO ₄ 2·5
	NaCl 2·5–5		NaCl 5–10		NaCl 7–12

Excessive amounts of any of the other common ions are best removed by passing the water through a mixed bed de-ionizer. This gives virtually pure water which can be treated in any way required, but it is a relatively expensive process. An excess of iron and associated manganese can be rapidly removed by passing the aerated water through a bed of granular, part-calcined Dolomite—a mixture of chalk and magnesia—which acts as both flocculant and filter. Moderate amounts of iron are removed in the decarbonation process with lime. Traces of oil and objectionable flavours, such as may be produced as a result of chlorination, are removed by passing the water through a bed of granular activated carbon. Treatments of this nature are required exceptionally and are therefore of minor importance.

sulphate, since the dry, bitter flavour of pale ales requires the sulphate/chloride ratio to be about 2/1, and the full, sweeter flavour of the mild ales needs a ratio of about 2/3. This is a generalization, and where the taste is for a rather sweeter pale ale than in the past, the ratio should probably be nearer 3/2 than 2/1. The soft flavour of stouts requires little, if any, sulphate, and the calcium will be present principally as chloride. Sodium chloride is responsible for part of the chloride in mild ales and stouts, and to a smaller extent in pale ales, where a large proportion would bring out a somewhat harsh hop flavour. If the liquor contains any appreciable amount of sodium as sulphate, it is advisable to replace part of what would normally be added as sodium chloride by calcium chloride or potassium chloride. It is open to doubt whether any magnesium

need be added, since the malt probably supplies all that the yeast requires, but many brewers prefer to make sure by bringing the magnesium content of the liquor up to about 0.5 grains per gallon. These recommendations for the composition of brewing liquors are summarized in Table II.

Readily soluble calcium and magnesium salts can be added to the liquor tank, always before decarbonation if this is carried out. Gypsum may also be added here provided it is given proper opportunity to dissolve, or it may be mixed with the grist in the grist case. Sodium or potassium chloride is usually added in the copper since its function is mainly one of flavour. Table III shows the

malt and is extracted early in the mash, *i.e.*, it is run off mainly in the strong wort. This means that when dealing with partigyles or splitting a length among two or three coppers, care must be taken not to get the chloride unevenly distributed between separated portions of the same brew, or the attention given to the balance of ions will be wasted.

Developments over the last few years have been towards simplification of the means whereby the treatment is applied. If the water supply to the brewery needs decarbonating, it is worth considering the use of special plant for the purpose and passing all the incoming water through it. The de-

TABLE III
EQUIVALENCE VALUES OF SOME LIQUOR SALTS

Anhydrous salt	Commercial form	Quantity = 1 grain per gallon	Proportions of ions
CaSO ₄	Gypsum, CaSO ₄ ·2H ₂ O	0.65 lb./100 brl.	Ca 3/SO ₄ 7
MgSO ₄	MgSO ₄ ·7 H ₂ O	1.05 lb./100 brl.	Mg 2/SO ₄ 8
NaCl	NaCl	0.51 lb./100 brl.	Na 4/Cl 6
CaCl ₂	Solution, sp. gr. 1360/1360	1.1 pints/100 brl.	Ca 3.6/Cl 6.4

forms in which the commercial salts are added, the amounts in lb. per 100 brl. which are equivalent to 1 grain per gallon of the pure anhydrous salt and the proportions by weight of the ions in each salt.

The suggestions that have been made as to liquor composition are intended only as a general guide. A brewer should try variations to discover what suits his process best and gives him the flavour he wants in his beers. He must remember that the character of a beer is influenced more by the *balance* of ions in the liquor than by the amount of any one of them. He has also to remember that an appreciable contribution to the chloride in his beer comes from the

carbonated water could then be used as it is for moderate heat processes such as cask washing and pasteurizing, without risk of scaling-up the pipelines and nozzles; it could be softened further, if necessary, for use in boilers and bottle washers; and it could be suitably hardened for use as brewing liquor. The hardening process, like the decarbonation, can be automatic if it is applied in the form of two metered solutions, one supplying chloride and the other sulphate. Alternatively, a simple basic treatment can be added to the decarbonated water, adjustment for pale ales being made by adding gypsum to the grist case, and for mild ales by adding sodium or potassium chloride to the copper.