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WASTE HAZARD PROPERTIES HP 4 'IRRITANT' AND HP 8 'CORROSIVE' BY PH, ACID/BASE BUFFER CAPACITY AND ACID/BASE CONCENTRATION

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ABSTRACT

European "Technical Recommendations" have proposed, with the use of substance concentrations, the use of a pH (≤ 2 or ≥ 11.5) to classify waste for the hazard properties HP4 'Irritant' and HP8 'Corrosive'. The document add unfortunately that the buffer capacity must be "not low" to classify as hazardous. Buffer capacity refers to a 2018 UK classification guide referring to the 'corrosive' level of a method proposed in 1988 for substances and preparations but not retained in EU regulations, but well in its Guidance. The product method uses the pH unclearly associated or not to a 1% concentration. The different methods of classifying products and wastes in terms of corrosivity or irritation are expressed as acid/base concentration and compared. The "corrosive" level of 1988 corresponds to an average strong acid/base concentration $\geq 14.4\%$, i.e. 14 times less severe than CLP (acid/base concentration $\geq 0.44-0.15\%$ for pH only or $\geq 1\%$ for pH and concentration). The "pH only" method corresponds to the lowest concentration of acid/base and is the most severe. These methods were applied to five hazardous alkaline wastes (pH ≥ 11.5). The "pH only" method is the only that classifies all waste in accordance with the European List of Waste. To avoid innovation and divergence between products and waste, it seems preferable to use the product regulations "pH only" or eventually "pH and concentration" for HP4 and HP8. Fortunately, the elimination of the danger HP 4 and HP 8 from acidic or alkaline waste can be obtained by neutralization, including for alkaline wastes with CO_2 .

1. INTRODUCTION

The waste hazard properties HP 4 'Irritant' and HP 8 'Corrosive' are assessed by concentrations of substances classified with hazard statement codes H314 1A or 1B or 1C, H315, H318 and H319, and the corresponding concentration limits (EU 2014). Further, European technical guidelines have recently also proposed the use of pH (≤ 2 or ≥ 11.5) and of acid / base buffer capacity to classify waste for the properties HP 4 and HP 8, "where the waste is not 'Irritant' as a result of the known substances and some substances are still unknown" (EU 2018). The buffer capacity limit is not given. However, it is suggested to refer to a classification guide from the United Kingdom (UK 2018), referring to a method proposed by the soap and detergent industry for substances and mixtures in the UK in 1988 (Young et al. 1988, 1994).

The UK soap and detergent industry developed a method for substances and mixtures, whose irritant or corrosive action through the skin is caused by acidity (pH ≤ 4) or alkalinity (pH ≥ 10) associated with a significant buffer

capacity. This combination of pH and buffering capacity is adjusted in order to correspond to experimental data of the two reference methods of that time (i.e. by calculation with the "R" system and by animal test), and to expert evaluations. This method classifies substances and mixtures into three levels: unclassified, irritant (low level) and corrosive (high level). The original method proposed in 1988 is presented and discussed using the raw data from the original publication.

The later European Regulation for the classification, labelling and packaging of substances and mixtures in Europe (CLP 2008) uses the United Nations Global Harmonized System, thus referring to the hazard statements codes "H" of substances and other classification methods by calculation. Additionally, when the substances are not known in the mixture, mixtures are classified for hazard as "Skin corrosives (category 1)" and "Serious eye damage (category 1)", if the pH is ≤ 2 or ≥ 11.5 , and the acid or base concentration is $\geq 1\%$. The classification of Young et al. (1988) has not been directly included in the CLP but is proposed in the Guidance of the CLP (ECHA 2017).

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As mentioned above, a communication from the European Commission (Technical Recommendations, EU 2018) suggests combining the pH limits of ≤ 2 and ≥ 11.5 of CLP combined with the "non-low" buffer capacity of waste (waste then classified as hazardous HP 8 'Corrosive') or "low" (waste then classified non-hazardous HP 8, but can be classified HP 4), according to the aforementioned UK Guide. The threshold for buffer capacity between non-low and low values is not indicated, but it is suggested to refer to the UK guide, i.e. to the "corrosive" limit set by the Young's classification.

In this paper, the Technical Recommendations (with some hypotheses) are expressed in terms of pH and acid or base concentration (rather than a combination of pH and buffer capacity) and are compared to the CLP Regulation. Five wastes are classified in the two systems and compared. The question of the reference method for the comparison of conventional classification methods, as for HP 14 'Ecotoxic' by list of waste, by calculation and by test, is discussed.

In supplementary information, (i) a simple method for determining the concentration of strong acid or base of a waste, (ii) the classification of lime, (iii) the harmonised classification of the main acids and bases that can be present in waste, and (iv) a list of acids and bases with their pKa are proposed.

2. MATERIAL AND METHODS

2.1 The classification by composition in substances of products (EU 2008) and waste (EU 2014)

The classification of substances and mixtures (called here "products") for Corrosion and Irritancy by composition in substances (CLP 2008) is done by route (eye / skin) and intensity in the route (irritation / corrosion). On the contrary, wastes are classified by intensity: low intensity HP 4 (route: skin and eye) and high intensity HP 8 (route: skin) (Table 1). There is no categories correspondence. The only matching calculation rule is highlighted in blue in the table. It can be useful to have gradual HP 8 "strong" and HP 4 "weak" with the same hazard statement codes (the only case in

the HPs) for the management of hazardous waste by the risk, here graduated.

2.2 Classification rules by pH, buffer capacity, and acid or base concentration limits (skin and eye corrosion and irritation)

For products, there are additional rules of pH and acid / base concentration for non-additives substances (CLP 2008, Table 3.2.4): the generic concentration limits of ingredients of a mixture for which the additivity approach does not apply, that trigger classification of the mixture as corrosive/irritant to skin are: Acid with $\text{pH} \leq 2$, concentration $\geq 1\%$ (Category 1), and Base with $\text{pH} \geq 11.5$, concentration $\geq 1\%$ (Category 1). The same system applies for eye exposure. It is not clear (including in the Guidance – ECHA 2017) if the pH and concentration conditions have to be fulfilled simultaneously (AND) or not (OR).

For wastes, the Commission Communication on technical recommendations concerning the classification of waste (EU 2018) proposes a flowchart for the classification of waste according to HP 4 and HP 8 which is based firstly on the knowledge of the substances of the waste, then secondly on taking into account the pH (≤ 2 and ≥ 11.5) and the buffering capacity, and thirdly, the performance of in vitro tests:

Where the waste is not 'Irritant' as a result of the known substances and some substances are still unknown, the pH value of the waste should be used for assessment (Figure 10). A waste with a $\text{pH} \leq 2$ or ≥ 11.5 should generally be considered HP 8 Corrosive unless both:

- an acid or alkali reserve test suggests that the classification as 'Corrosive' is not warranted, and
- further in vitro testing, or existing human experience and animal data from single or repeated exposure has confirmed that classification as neither 'Irritant'/'Corrosive' applies.

But the Figure 14 (p 107) of that document add unfortunately that the buffer capacity must be "not low" to

TABLE 1: Classification of substances and mixtures ("products") and waste by hazard statement of substances and calculation. The only matching rule is highlighted.

Category (Severity) → Route of exposure ↓	Hazard Statement Codes		PRODUCTS	Hazard classes of mixtures	
	High level Cat. 1	Low level Cat. 2		High level	Low level
Dermal	H314 Skin Corr. 1A, 1B, 1C	H315 Skin irrit. 2	→	« Skin corrosion» $\sum \text{H314 1A} \geq 5\%$ $\sum \text{H314 1A, 1B} \geq 5\%$ $\sum \text{H314 1A, 1B, 1C} \geq 5\%$	« Skin irritation» H 314 1A,1B, 1C $\geq 1\%$ but < 5%. $\sum [10*(\text{H314 1A, 1B, 1C}) + \text{H315}] \geq 10\%$
Eye	H318 Eye dam. 1	H319 Eye irrit. 2	→	« Serious eye damage» $\sum (\text{H314 1A, 1B, 1C} + \text{H318}) \geq 3\%$	« Eye irritation» $\sum [(10*\text{H314 1A, 1B, 1C}) + \text{H315} + (10*\text{H318}) + \text{H 319}] \geq 10\%$
WASTE	↓	↓			
Waste Hazard Property	HP 8 'Corrosive' $\sum \text{H314 1A, 1B, 1C} \geq 5\%$	HP 4 'Irritant' $\sum \text{H314 1A} \geq 1\%$ $\sum \text{H318} \geq 10\%$ $\sum (\text{H315 and H319}) \geq 20\%$			

classify as hazardous. The buffer capacity refers to the UK Guide, citing Young et al. (1988). There is no concentration limit of buffer capacity indicated in this European document.

Negative conditions should be avoided in classification wording since they are more difficult to understand and to implement. We understand the conditions mentioned above as:

- if $\text{pH} \leq 2$ or ≥ 11.5 , the waste is classified HP 8;
- if $\text{pH} \leq 2$ or ≥ 11.5 AND the buffer capacity is low AND a biotest is negative, the waste is NOT classified HP 8;
- if $\text{pH} \geq 2$ or ≤ 11.5 , the waste is NOT classified HP 8.

A recent study has shown that there is no solution with biological tests up till now (Concawe, 2020), so that option will not be studied here. Even more, concentration limits to assess the result of tests are nor proposed neither validated by comparison with a reference method for waste. Some possible outdated options can be found

in OECD (1981). The above conditions can then be re-phrased as:

- if $\text{pH} \leq 2$ or ≥ 11.5 , the waste is classified HP 8;
- if $\text{pH} \leq 2$ or ≥ 11.5 AND the buffer capacity is high, the waste is classified HP 8;
- if $\text{pH} \geq 2$ and ≤ 11.5 , the waste is NOT classified HP 8.

How the first two parallel conditions inter-relate? That question will be clarified in this paper (Table 2).

The buffer capacity is a measure of the concentration of dissociated acid or base in the mixture at a given pH, by titration to a given pH. In this document, the « acid alkali reserve » of Young et al. is converted in buffer capacity (BC): 1 unit Acid Alkaline Reserve AAR = 1 g NaOH/100 g = 0.25 mol H⁺ or OH⁻/kg = 0.25 BC (mol/kg). The buffer capacity is measured by titration with a strong base or a strong acid, up to a given pH. Young et al. chose pH 4 for the acid domain and pH 10 for the alkaline domain. It is considered that there is no irritancy or corrosiveness by acidity or al-

TABLE 2: Classification of substances and mixtures (“products”) and waste by pH, acid/base concentration, and acid/base buffer capacity.

Hazard	Domain	Conditions to be fulfilled simultaneously		
		pH	Concentration	Buffer capacity (mol H ⁺ or OH ⁻ /kg)
Products (CLP 2008)				
Skin corrosion, Severe eye damage (high level)	Acid	≤ 2	AND? OR? $\geq 1\%$	-
	Alkaline	≥ 11.5	AND? OR? $\geq 1\%$	-
Products (ECHA Guidance 2017 3.3.3.2.1.1.)				
Skin corrosion, Severe eye damage (high level)	Acid	≤ 2	-	-
	Alkaline	≥ 11.5	-	-
Waste (EC 2018)				
HP 8 ‘Corrosive’	Acid	≤ 2	-	AND « Not low » as in UK 2018
	Alkaline	≥ 11.5	-	AND « Not low » as in UK 2018
HP 4 ‘Irritant’	Acid	≤ 2	-	→ classify by HP 8
	Alkaline	≥ 11.5	-	→ classify by HP 8
Waste (UK 2018)				
HP 8 ‘Corrosive’	Acid	≤ 2	-	AND $\text{pH} - 1/3 \text{BC}_{\text{pH}4} \leq -0.5$ (high level of Young)
	Alkaline	≥ 11.5	-	AND $\text{pH} + 1/3 \text{BC}_{\text{pH}10} \geq 14.5$ (high level of Young)
HP 4 ‘Irritant’	Acid	≤ 2	-	→ classify by HP 8
	Alkaline	≥ 11.5	-	→ classify by HP 8
Products (Young et al. 1988)				
Expression in buffer capacity*:				
Skin corrosive (high level)	Acid	≤ 4	-	$\text{pH} - 1/3 \text{BC}_{\text{pH}4} \leq -0.5$
	Alkaline	≥ 10	-	$\text{pH} + 1/3 \text{BC}_{\text{pH}10} \geq 14.5$
Skin irritant (low level)	Acid	≤ 4	-	$\text{pH} - 2/3 \text{BC}_{\text{pH}4} \leq 1$
	Alkaline	≥ 10	-	$\text{pH} + 2/3 \text{BC}_{\text{pH}10} \geq 13$
Original expression in acid-alkaline ratio AAR*				
Skin corrosive (high level)	Acid	≤ 4	-	$\text{pH} - 1/12 \text{AAR}_{\text{pH}4} \leq -0.5$
	Alkaline	≥ 10	-	$\text{pH} + 1/12 \text{AAR}_{\text{pH}10} \geq 14.5$
Skin irritant (low level)	Acid	≤ 4	-	$\text{pH} - 2/12 \text{AAR}_{\text{pH}4} \leq 1$
	Alkaline	≥ 10	-	$\text{pH} + 2/12 \text{AAR}_{\text{pH}10} \geq 13$

* Buffer capacity BC (mol H⁺ or OH⁻ / kg) = 4 x Acid Alkaline Ratio AAR (g NaOH / 100 g) (one unit AAR = 1 g NaOH / 100 g = 10 g NaOH / kg = 0.25 mol OH⁻ / kg = ¼ unit BC)

kalinity between pH 4 and pH 10. It should be noted that these pHs are not the ones chosen for classification by the CLP and for waste.

2.3 Determination of the concentration limits of the pH and buffer capacity method by the soap and detergents industry of UK

Numerous substances and mixtures were classified according to the two reference methods at that time: substance properties and concentration (with the previous "risk phrase R" system and their concentration limits of the Dangerous Preparation Directive EEC 1967), and animal test (rabbit eye damages). Their pH and buffer capacity were also measured. Empirical concentration limits combining pH and buffer capacity were then adjusted to the reference classification data (Figure 1). The obtained correspondence or correlation with the two reference methods is convincing (Figure 2).

2.4 Reference method for the assessment of the buffer capacity classification method, and expression of the pH and the BC in strong acid/base concentration

Classifications are conventional and can always be discussed as they set punctual limits to continuous variables. New classification systems can be built in line with refer-

ence system(s). On the issue of the reference method when building a new classification system, Jung et al. (1988) adjusted empirically their concentration limits to the reference methods of their time by concentration and by animal tests. For the waste hazard property HP 14, concentration limits are proposed for ecotoxicological tests (without pH adjustment) by matching with classification by the European list of waste of absolute non-hazardous (with control of chemical composition) and hazardous waste (Hennebert 2018). The question is similar here. To assess the Young method, we chose as reference method the CLP because it is in fact the Global Harmonised System for chemicals of the United Nations and has been built by a high-level global expertise in toxicology.

In order to compare methods, their expression must be harmonised. The pH, the acid and base concentration, and the buffer capacity are functions of each other. The correspondences are easily calculated under the assumption that all the acid or the base of the product or the waste is in solution in the suspension in water used for the measurement of the pH and the titration of the buffer capacity, or equivalently the acids and bases are "strong". For $pH \leq 2$ and ≥ 11.5 , the acids and bases are always "strong". A list of acids and bases with their pKa (the pH at which they are 50% dissociated) is given in the supplementary information section. From the pH to the concentration, the normal concentration of acid or base in the 10 l leachate per kg solid waste is equal to or greater than $\log(-pH) = \log(-2)$ for acids and $\log(-pOH) = \log(-2.5)$ for bases. The result in normal concentration is expressed per kg waste. From the BC to the concentration, the BC (mol H⁺ or OH⁻/kg) is a normal concentration. The normal concentration is multiplied by the mass of one equivalent (the molar mass divided by the number of equivalent) to obtain a weight concentration. These calculations have been done with 3 strong acids and 3 strong bases. CaO dissolves only partly at pH > 12 and more precise calculations were done with Minteq (free reference software supported by USEPA). The calculated concentration levels are lower than the maximum solubilities in water at 25°C (Minteq V3 calculations, not shown), excepted for the case of lime Ca(OH)₂. In the acid domain, the buffer capacity of HNO₃, HCl, H₂SO₄ (mean 44.4 g/mol H⁺) is 44.4 g/kg or 4.44% w/w for 1 mol H⁺/kg. In the alkaline domain, the buffer capacity of NaOH, KOH, Ca(OH)₂ (mean 49.5 g/mol OH⁻) (use of Minteq V3 for partial dissolution of Ca(OH)₂) is 49.5 g/kg or 4.95% w/w for 1 mol OH⁻/kg. The mean BC of acids and bases is 46.9 g/kg = 4.69% w/w for 1 mol H⁺ or OH⁻/kg.

3. RESULTS

3.1 Comparison of the acid/base concentration proposed for waste classification (EU 2018) and for products (CLP 2018)

The buffer capacity (BC) and its relationship with the pH of Young – UK Guide– EU Recommendations are expressed in concentration of strong acids and bases (Table 3, Figure 3). Reversely, the acid and base concentrations of the CLP can be expressed in pH (with a solid-to-liquid ratio of 10 l/kg for solids, as in the leaching standard EN 12457-

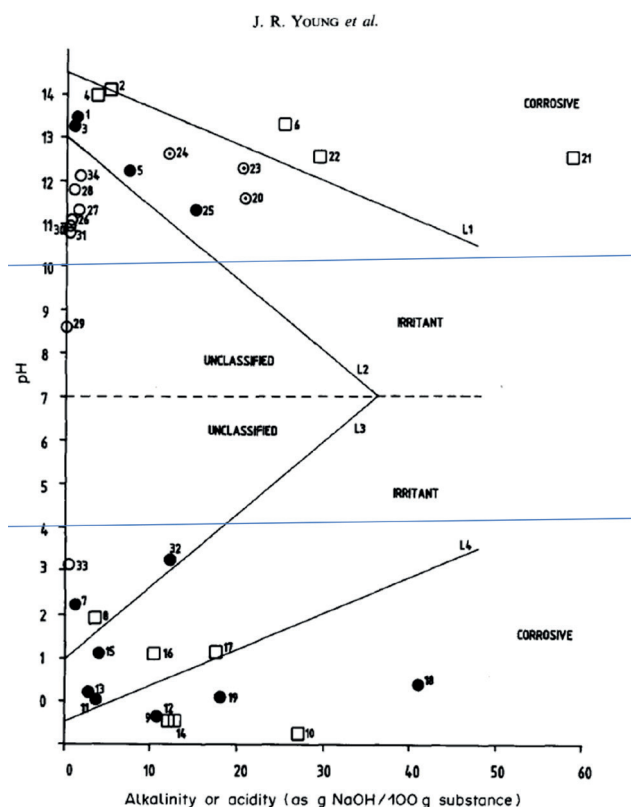


FIGURE 1: Buffer capacity and pH of 34 substances, classification by the R regulation of 1967 (black balls: irritant, white squares: corrosive), and proposed pH and buffering capacity limits (black straight lines) (Young et al. 1988). Non-classifying limits of pH = 4 and pH = 10 are added as blue vertical lines – the labels "irritant" should move to the left and to the right.

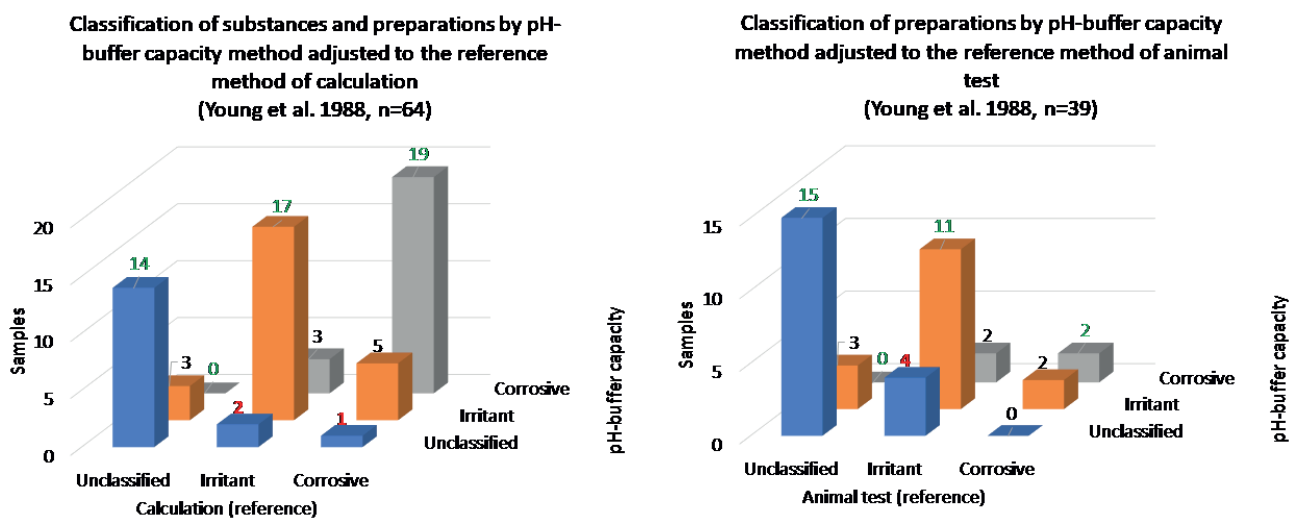


FIGURE 2: Correspondence between two reference methods and the adjusted pH-buffer capacity of substances and mixtures (recalculated from Young et al. 1988). The number of samples of each category is labelled.

2) and buffer capacity. The 'irritant domains' of Young are not used in the recommended waste classification and are not presented in the table. The 'corrosive domains' of Young corresponds to BCs > 3 mol/kg, by the presence of strong acids and bases), to a concentration of strong acids $\geq 15.2\%$ and a concentration of strong base $\geq 13.6\%$, and to the pHs ≤ 0.5 or ≥ 13.1 . The mean concentration of acid and bases is 14.4%.

The waste classification conditions for HP 8:

- if $\text{pH} \leq 2$ or ≥ 11.5 , the waste is classified HP 8;
- if $\text{pH} \leq 2$ or ≥ 11.5 AND the buffer capacity is high, the waste is classified HP 8;
- if $\text{pH} \geq 2$ and ≤ 11.5 , the waste is **NOT** classified HP 8 by the pH.

Can then be rephrased as:

- if $\text{pH} \leq 2$ or ≥ 11.5 , the waste is classified HP 8;
- if $2 \leq \text{pH} \leq 11.5$, the waste is **NOT** classified for HP 8 by the pH (and the buffer capacity).

Named here "classification by pH only (BC de facto fulfilled)" since the condition of BC is always fulfilled when the conditions of pH are fulfilled, these re-expressed calculation rules have the important advantages of (i) chemical consistency, (ii) non-divergence between waste and product classification, and (iii) simplicity.

3.2 Comparison of the acid/base concentration proposed for waste classification (EU 2018) and the harmonised classification of strong acids and bases (CLP 2018)

The detailed hazard statements of the acids and bases that can be found in waste are given in Supplementary Information, with a list of pKa and pKb of numerous acids and bases (the pH with 50% dissociation of the acid and base). For three common strong acids and base, the hazard statement code, the waste hazard calculation, and the concentration limit are presented in Table 4. The concentration limits for the waste HPs are 1% for HNO_3 , H_2SO_4 , NaOH and KOH, 5% for HCl, and 10% for $\text{CaO}/\text{Ca}(\text{OH})_2$. It

TABLE 3: The pH, the acid/base concentration, and the buffer capacity (BC) for the classification of products (skin corrosion, severe eye damage) and the recommended classification of waste for the hazard property HP 8 'Corrosive'. Yellow: classification rule, orange: calculated corresponding pH, concentration and BC.

Classification	Domain	Rules (yellow)			Corresponding calculated pH, concentration and BC for direct comparison		
		pH	Concentration limit (data)	BC mol/kg	pH 10 l/kg	Concentration limit	BC mol/kg (up to pH 4 or down to pH 10)
Products CLP High level	Acid	≤ 2		Undefined	≤ 2	$\geq 0.44\%$	≥ 0.10
	Alkaline	≥ 11.5		Undefined	≥ 11.5	$\geq 0.15\%$	≥ 0.03
Products CLP High level	Acid		$\geq 1\%$	Undefined		$\geq 1\%$	≥ 0.21
	Alkaline		$\geq 1\%$	Undefined		$\geq 1\%$	≥ 0.23
Product Young 1988 Corrosive	Acid	≤ 4	Undefined	$\text{pH} - 1/3$ $\text{BC}_{\text{pH4}} \leq -0.5$	≤ 0.5	$\geq 15.2\%$	≥ 3.06
Waste Recommended UK 2018 HP 8 Recommended EU 2018 HP 8	Alkaline	≥ 10	Undefined	$\text{pH} + 1/3$ BC $\text{pH}_{10} \geq 14.5$	$\geq 13.1^*$	$\geq 13.6\%$	≥ 3.05

* Note: NaOH, KOH = pH 13.5, Ca(OH)2 (partial dissolution) = pH 12.4, mean pH = 13.1

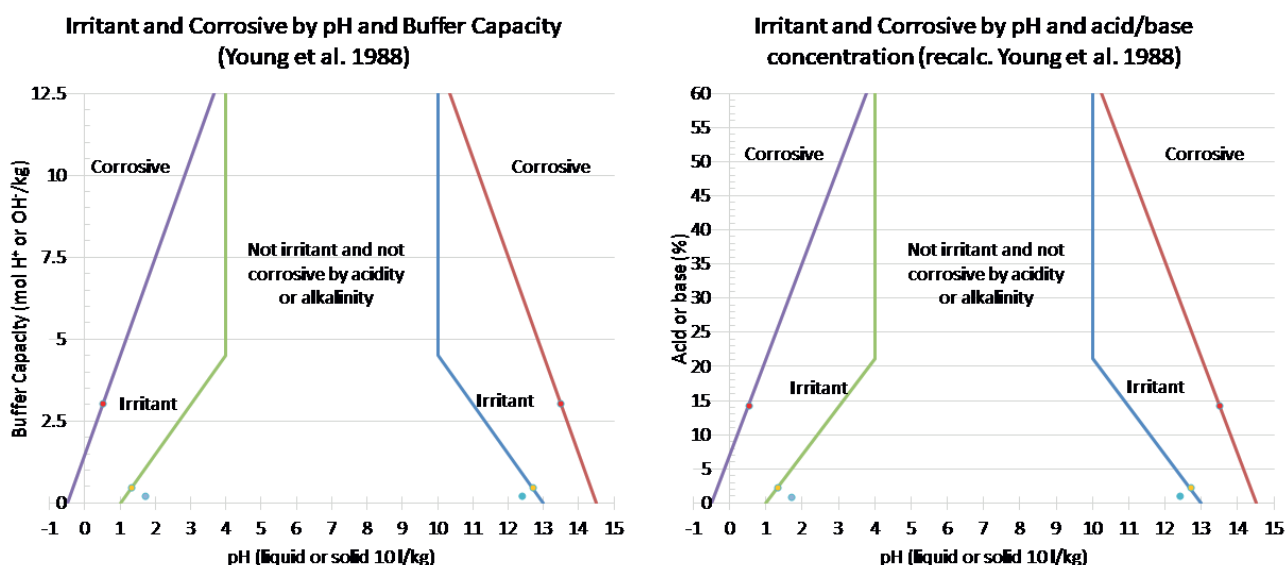


FIGURE 3: The pH - buffer capacity domain of irritancy and corrosiveness of Young et al. 1988, expressed in buffer capacity (left) and acid/base concentration (right). The blue points correspond to the classification of products in the CLP, and the yellow and red points to classification as irritant and corrosive by Young et al. (1988).

should be noted that these substances (excepted CaO and Ca(OH)₂) have specific concentration limits in the product CLP regulation (with graduated concentrations and hazard statements, the lowest being for HNO₃ and H₂SO₄ 5%, HCl 10%, NaOH and KOH 0.5%) (see supplementary information). The specific concentration limits of substances do not apply to waste. In summary, all these concentrations are lower than the 14.4% suggested by Young et al. (1988) and proposed to be used in waste classification (EU 2018), the latest being here also less severe.

3.3 Correspondence of classification with the CLP and the EU Technical Recommendations for 5 wastes

The pH (L/S = 10 l/kg) and the buffer capacity of five alkaline waste (fly ashes and air pollution control residues) have been measured. The buffer capacity is converted into base concentration using 0.044 kg acid/equivalent, as explained above. These wastes were classified by (i) the product or waste method by pH only (BC de facto fulfilled) (CLP 2008) and (ii) by pH and concentration of 1% (CLP 2008), and (iii) by the Technical Recommendations for waste classification (EU 2018) (Table 5, Figure 4). The two last classification systems correspond for low and high pHs and BCs (sample 1 and 3, 4, 5), but not for the intermediate pH and BC (sample 2).

The classification with pH only (BC de facto fulfilled) classifies all waste HP 8. pH and 1% concentration system is less severe (sample 1 is not classified hazardous). The BC system is the less severe (samples 1 and 2 are not classified hazardous). It should be noted that the air pollution control residues are classified as “absolute hazardous” in the European List of Waste. The classification with the pH only (BC de facto fulfilled) match with that reference method.

3.4 Correspondence of the different classification systems for irritancy and corrosiveness

The chronology and the correspondences and differences of the systems that were used and are used are presented in Figure 5. The proposed system for waste uses a concentration of 14% of acid or base, which is an obvious discrepancy (very highly less severe) between products and waste, not favourable to the smooth flow between waste status and product status that should exist in the circular economy. In order not to innovate and create a new divergence between products and waste, it seems preferable to use the product regulation for waste classification for HP 4 and HP 8.

Classifying waste with a concentration of acid or base > 1% or lower with the “pH only” rule rather than 14% as hazardous is a supplementary burden for their management.

TABLE 4: Concentration limit of strong acids and bases by the harmonised classification of substances of the CLP and the classification rules for HP 4 and HP 8.

Acid domain	Alkaline domain	Hazard statement code	Waste Hazard property, classification rule and concentration limit	Lowest Concentration limit for hazardous waste
HNO ₃ , H ₂ SO ₄	NaOH, KOH	H314 1A	HP 4 A: $\sum H314\ 1A \geq 1\%$ HP 8 A: $\sum H314 \geq 5\%$	HP 4: 1%
HCl		H314 1B	HP 8 A: $\sum H314 \geq 5\%$	HP 8: 5%
	CaO, Ca(OH) ₂	H318 H315	HP 4 B: $\sum H318 \geq 10\%$ HP 4 C: $\sum H315$ and $H319 \geq 20\%$	HP 4: 10%

TABLE 5: Analyses and classification of 5 waste (fly ashes, air pollution control residues) with the waste pH system, the product system and the proposed BC waste system (BC = buffer capacity).

Sample	Analyses		Calculated strong base concentration corresponding to the measured BC (0.044 kg/eq)	Waste classification by pH (EU Recommendations 2018) or Product classification by pH (CLP 2008, ECHA 2017) = classification by pH only (BC de facto fulfilled)	Product classification by pH AND 1% concentration (CLP 2008)	Classification by pH AND pH+BC high limit (UK guide 2018 suggested in EU Recommendations 2018)
	Initial pH	BC _{pH10} (mol/kg)				
1	11.7	0.05	0.2%	HP 8	Unclassified	Unclassified
2	12.4	0.7	3.1%	HP 8	Skin corrosion, Severe eye damage (high level)	Unclassified
3	12.6	7.1	31.5%	HP 8	Skin corrosion, Severe eye damage (high level)	HP 8
4	12.6	8.7	38.5%	HP 8	Skin corrosion, Severe eye damage (high level)	HP 8
5	12.8	7.4	32.9%	HP 8	Skin corrosion, Severe eye damage (high level)	HP 8

Fortunately, the elimination of the hazardous nature HP 4 and HP 8 from acid or alkaline waste can be obtained by neutralization (possibly by waste of the other acid/alkali domain), as done in specialised hazardous waste management facilities, before stabilisation/solidification and landfilling in dedicated landfills. Neutralisation of acid waste or alkaline waste is not done to dilute the hazardous concentration and to change the classification and the management of the waste to a lower demanding level, but well to destroy the hazard, as well as incineration for organic substances.

Another option for alkaline waste is the (natural) carbonation by atmospheric CO₂ in presence of soluble calcium, to precipitate the carbonate of the liquid phase to the solid phase and decrease the pH potentially up to the pH 8.5 (the pH of limestone in water) if the alkaline metals Na and K are washed out. This beneficial process is used for instance for the "maturation" of bottom ash from house-

hold waste incineration and the carbonation of red mud from alumina production.

4. CONCLUSIONS

The product system is not clear between two options: pH ≤ 2 or ≥ 11.5 OR concentration ≥ 1% (with a corresponding concentration of strong acid and base of 0.44 and 0.15%, respectively), or pH ≤ 2 or ≥ 11.5 AND concentration ≥ 1% (with a corresponding pH ≤ 1.7 or ≥ 12.4). It should be made clear what is the official option.

The "irritant" low level of Young's classification (1988, 1994), not proposed in the UK guide and EU recommendations, corresponds to pH ≤ 1.3 and ≥ 12.7, and average concentrations of acid and base ≥ 2.3%, which is a classification approach half as severe as the CLP.

The "corrosive" high level of Young et al. proposed for waste classification as a second compulsory condition (EU 2018) corresponds on average with 3 strong acids (HCl, HNO₃ and H₂SO₄) and 3 strong bases (NaOH, KOH and Ca(OH)₂) to pH ≤ 0.5 and ≥ 13.5, respectively, and at an average to an acid and base concentrations ≥ 14.4%. Therefore, Young's classification is very much less severe than the product's system CLP: much more acid or base is necessary to be hazardous. That condition in the "Technical Recommendations" should be withdrawn.

These propositions have been applied to five air pollution control residues (pH ≥ 11.5) which have been analysed and classified according to the different rules. These wastes are "absolute hazardous" in the European list of waste. The only method that classifies the five waste as HP 8 is the simplest one: pH ≤ 2 or ≥ 11.5. Addition of the requirement of a "not low" buffer capacity (corresponding to a concentration ≥ 14.4%) do not classify as hazardous two of the five wastes.

In order not to innovate and create a new divergence between products and waste (as observed in one of the five wastes studied), it seems preferable to use the simple product first option: pH ≤ 2 or ≥ 11.5.

Elimination of the hazardous nature HP 4 and HP 8 from acid or alkaline waste can be obtained by neutralization (possibly by other waste in specialised waste treat-

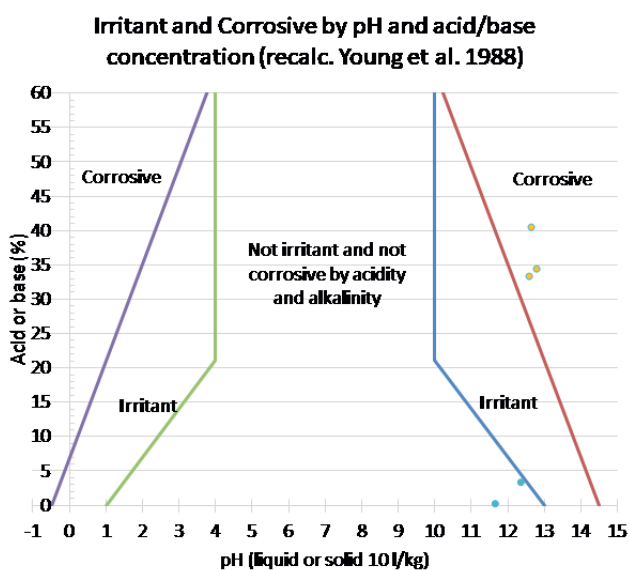


FIGURE 4: pH and base concentration of 5 wastes in the proposed classification system for waste (EU 2018).

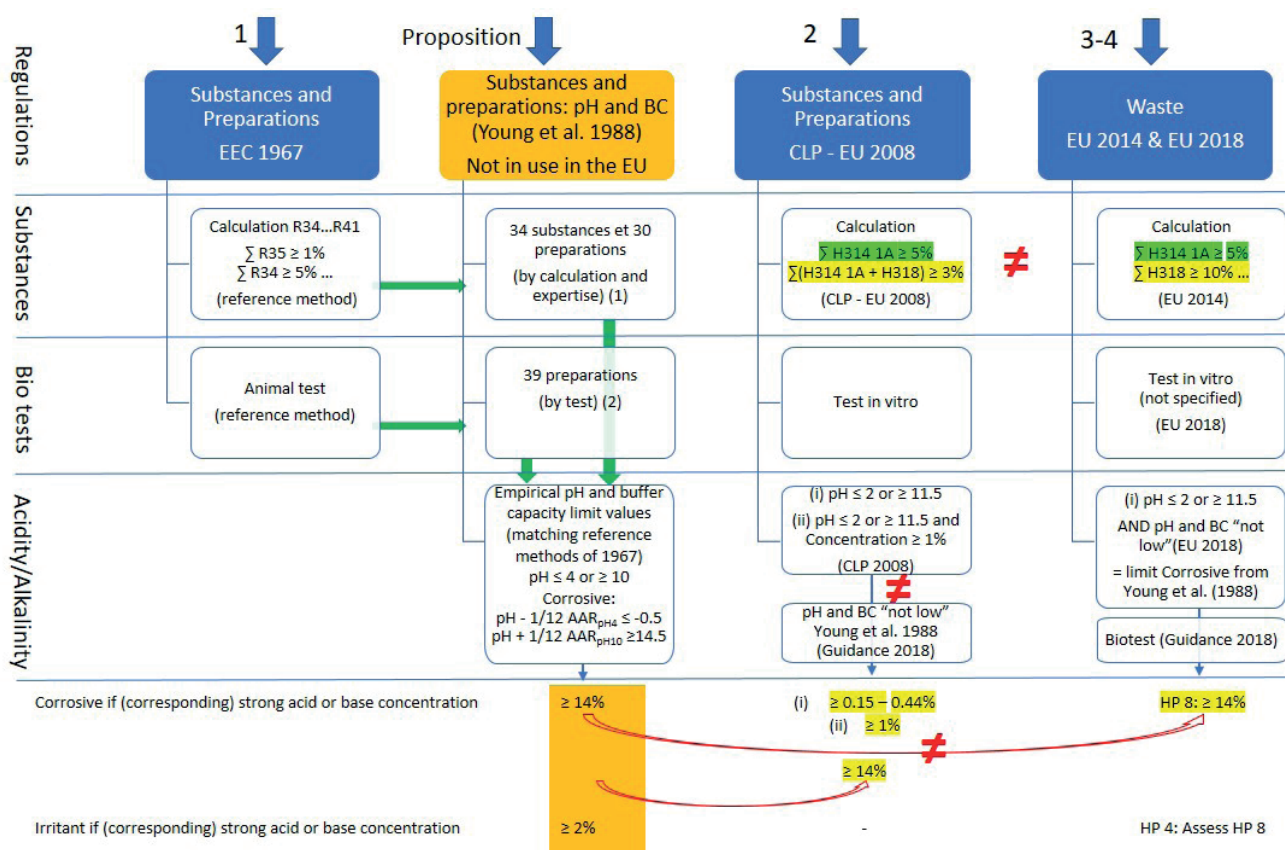


FIGURE 5: Regulations on corrosive and irritating for the skin and eyes products and waste. BC = buffer capacity. Large blue arrows: regulations in chronological order; green arrows: reference method and laboratory data used by Young et al. to derive pH-BC relationships; AAR: acid alkaline ratio, an old expression of buffer capacity; #: differences; green highlight: concordance; yellow highlight: differences.

ment facilities), including for alkaline waste by (natural) carbonation by atmospheric CO₂. This beneficial process is used for instance for the "maturation" of bottom ash from household waste incineration and the carbonation of red mud from alumina production.

A simple method determining the strong acid or base concentration of a waste is proposed in supplementary information.

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1. SUPPLEMENTARY INFORMATION

1.1 Proposal for a method measuring the concentration of strong acid or strong base in a waste

A method for products is described in OECD (2013). For waste, using classical waste methods, the concentration and identification of strong acids or bases can be done as follows:

1. Measurement of the pH of liquid waste or of a suspension in water of solid waste at 10 litres / kg of dry matter (EN 12457-2, without liquid / solid separation) after 1 h of equilibration;
2. If the pH ≤ 2 or ≥ 11.5 , measure the buffering capacity of the liquid waste or of the suspension of solid waste by titration with a base up to pH 4 or a strong acid up to pH 10, with 48 h. balancing (EN 14997 leaching at different pH, used in titration mode up to pH 4 or pH 10).
3. Preparation of a leachate (EN 12457-2 with liquid / solid separation) on a separate sample and measurement of pH, electrical conductivity, TOC, anions and leachable cations.

The quantity (in equivalent) of strong acid or strong base of the sample is equal to the buffering capacity of the sample up to pH 4 or pH 10. The nature of the acid (s) and bases is determined by the majority anions and cations measured in the leachate. The amount in acid or base equivalent is then expressed as a substance concentration, using the molecular weight and the number of acid or alkali equivalents of the substance (s) identified.

In a simplified mode (without determining the acid or the base):

1. Measure the pH
2. Measure the buffering capacity
3. Express the buffering capacity in concentration of acid or base by multiplying by the mass of an equivalent of acid or base chosen (1 mol H⁺ or OH⁻ / kg \approx 4.5% acid or base)
4. This approach does not give information on substances (with their specific approach like lime) and will not be available.

1.2 Special case of lime

1.2.1 Hazard statements for quicklime and slaked lime (self-classification) and (EC Technical Recommendations 2018)

The presence of free lime (quick or slaked) results in a pH of around 12.5. Quicklime and slaked lime are not classified by the CLP regulation. The data for self-classification are as follows (Table SI 6).

Waste containing 10% lime will therefore be classified HP 4 Irritant 'and waste containing 20% lime will be classified HP 4 'Irritant ' and HP 5 'Harmful - Single target organ toxicity / aspiration toxicity'.

Note: Absolute "non-hazardous" entries in the European list of wastes containing lime should not be reclassified by composition, such as steel mill slags.

1.3 Classification of main acids and bases (CLP)

The table shows the harmonized classification of strong acids and strong bases that may be present in the waste. The last column gives for information the specific concentration limits in preparations and substances, which do not apply to the classification of waste. For the same substance in a preparation, the hazard statements depend on the concentrations.

TABLE SI 6: Properties of quicklime and hydrated lime according to the registrants in the registration dossier with ECHA and classification rules and concentration limits applicable to waste.

International Chemical Identification	CAS No	Hazard Class and Category Code(s)	Hazard Statement Code(s)	Source	Concentration limits Waste 2014
calcium oxide	1305-78-8	Eye Dam. 1 Skin Irrit. 2 STOT SE 3 respiration	H318 H315 H335	https://echa.europa.eu/brief-profile/-/briefprofile/100.013.763	HP 4 Irritant: $\sum H318 \geq 10\%$ HP 4 Irritant: $\sum (H315 H319) \geq 20\%$ HP 5 STOT: max H335 $\geq 20\%$
calcium dihydroxide	1305-62-0	Eye Dam. 1 Skin Irrit. 2 STOT SE 3	H318 H315 H335	https://echa.europa.eu/brief-profile/-/briefprofile/100.013.762	HP 4 Irritant: $\sum H318 \geq 10\%$ HP 4 Irritant: $\sum (H315 H319) \geq 20\%$ HP 5 STOT: max H335 $\geq 20\%$

STOT = single target organ toxicity/aspiration toxicity

There is no harmonized classification for magnesium oxide, hydroxide and carbonate. By default, the hazard statements of the corresponding calcium species could be used (Table SI 7).

1.4 List of acids and bases and pKa and pKb

The pKa is the pH to which 50% of the acid or base is dissociated, or the pH of which the concentration of the acid form equals the concentration of the conjugate base. The basics of chemistry tell us that:

$$K_a = [A^-] [H^+] / HA$$

$$[H^+] = K_a [HA] / [A^-]$$

$$pK_a = \log [A^-] + \log [H^+] - \log [HA]$$

$$pH = \log [A^-] - \log [HA] - pK_a$$

The colors correspond to the extended pH ranges of one unit (acid / conjugate base ratio = 1/10, i.e. one logarithmic unit) (Table SI 8).

TABLE SI 7: Specific concentration limits in preparations and mixtures (harmonized classification of substances, CLP 2008).

Index No	International Chemical Identification	EC No	CAS No	Hazard Class and Category Code(s)	Hazard Statement Code(s)	Specific Conc. Limits, M-factors
017-002-01-X	hydrochloric acid ... %	231-595-7		STOT SE 3 Skin Corr. 1B	H335 H314	Skin Corr. 1B; H314: C ≥ 25% Skin Irrit. 2; H315: 10 % ≤ C < 25% Eye Irrit. 2; H319: 10 % ≤ C < 25% STOT SE 3; H335: C ≥ 10%
009-003-00-1	hydrofluoric acid ... %	231-634-8	7664-39-3	Acute Tox. 1 Acute Tox. 2 * Acute Tox. 2 * Skin Corr. 1A	H310 H330 H300 H314	Skin Corr. 1A; H314: C ≥ 7% Skin Corr. 1B; H314: 1 % ≤ C < 7% Eye Irrit. 2; H319: 0,1 % ≤ C < 1%
007-004-00-1	nitric acid ...%	231-714-2	7697-37-2	Ox. Liq. 2 Skin Corr. 1A	H272 H314	Ox. Liq. 2; H272: C ≥ 99% Ox. Liq. 3; H272: 65% ≤ C < 99% Skin Corr. 1A; H314: C ≥ 20% Skin Corr. 1B; H314: 5% ≤ C < 20%
015-011-00-6	phosphoric acid ... %, orthophosphoric acid ... %	231-633-2	7664-38-2	Skin Corr. 1B	H314	Skin Corr. 1B; H314: C ≥ 25% Skin Irrit. 2; H315: 10 % ≤ C < 25% Eye Irrit. 2; H319: 10 % ≤ C < 25%
016-020-00-8	sulphuric acid ... %	231-639-5	7664-93-9	Skin Corr. 1A	H314	Skin Corr. 1A; H314: C ≥ 15% Skin Irrit. 2; H315: 5% ≤ C < 15% Eye Irrit. 2; H319: 5% ≤ C < 15%
007-001-01-2	ammonia%	215-647-6	1336-21-6	Skin Corr. 1B Aquatic Acute 1	H314 H400	STOT SE 3; H335: C ≥ 5%
011-002-00-6	sodium hydroxide; caustic soda	215-185-5	1310-73-2	Skin Corr. 1A	H314	Skin Corr. 1A; H314: C ≥ 5% Skin Corr. 1B; H314: 2% ≤ C < 5% Skin Irrit. 2; H315: 0,5 % ≤ C < 2% Eye Irrit. 2; H319: 0,5% ≤ C < 2%
011-005-00-2	sodium carbonate	207-838-8	497-19-8	Eye Irrit. 2	H319	
019-002-00-8	potassium hydroxide; caustic potash	215-181-3	1310-58-3	Acute Tox. 4 * Skin Corr. 1A	H302 H314	Skin Corr. 1A; H314: C ≥ 5% Skin Corr. 1B; H314: 2% ≤ C < 5% Skin Irrit. 2; H315: 0,5% ≤ C < 2% Eye Irrit. 2; H319: 0,5% ≤ C < 2%

TABLE SI 8: XX

Acid	Conjugated base	pKa	Domain pH ≤ 2 or ≥ 11.5 (CLP), domain ≤ 4 or ≥ 10 (Young et al. 1988)	Note
HI	I-	-11		Those acids should be considered for HP 4 and HP 8
HBr	Br-	-9		
HClO4	ClO4-	-8		
HCl	Cl-	-7		
H2SO4	HSO4-	-3		
HN03	NO3-	-1.64		
H2CrO4	HCrO4-	-1		
H3PO2	H2PO2-	1.1		
H2C2O4	HC2O4-	1.2		
H3PO3	H2PO3-	1.8		
HSO4-	SO4--	1.9		
			pH 2	
H3PO4	H2PO4-	2.1		
H3AsO4	H2SO4-	2.2		
HF	F-	3.2		Those acids should be considered for HP 4 and HP 8
HNO2	NO2-	3.4		
HCOOH	COOH-	3.8		
			pH 4	
C6H5COOH	C6H5COO-	4.2		
CH3COOH	CH3COO-	4.75		
CH3CH2COOH	CH3CH2COO-	4.9		
H2PO3-	HPO3--	6.2		
H2CO3	HCO3-	6.33		
HCrO4-	CrO4--	6.5		
H2AsO4-	HAsO4--	7		Those acids should be considered for HP 4 and HP 8
H2S	HS-	7		
H2PO4-	HPO4--	7.2		
NH4+	NH3	9.2		
HCN	CN-	9.3		
H3AsO3	H2ASO3-	9.5		
H2SiO3	HSiO3-	9.9		
			pH 10	
C6H5OH	C5H5O-	10		
HCO3- *	CO3--	10.33		
			pH 11.5	Those bases should be considered for HP 4 and HP 8
HAsO4--	AsO4--	11.5		
Ca(OH)+ **	Ca++ + OH-	11.57		
HPO4--	PO4--	11.9		
Ca(OH)2 **	Ca(OH)+ + OH-	12.63		
HS-	S-	13		
NaOH	Na+ + OH-	14.56		
KOH	K+ + OH-	14.7		

* Na2CO3 saturated in deionised water = pH 11.42 (Minteq V3 calculation)
 ** Ca(OH)2 (Portlandite) saturated in deionised water = pH 12.44 (Minteq V3 calculation)