

Proposed Methodology for Inter-Comparison of Steel Rebar Properties from Different Manufacturing Sources

N. Karar* & Vipin Jain

CSIR-National Physical Laboratory, Dr KS Krishnan Road, New Delhi, 110012, India

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We propose a new method for checking steel quality and repeatability in microstructure using a combination of X-Ray diffraction (XRD) and Raman Spectral data analysis methodology¹. Here, we discuss the case of steel rebars. We consider 23 different brands of steel rebars from across India. We did an inter-comparison of their elemental chemical composition using X-ray fluorescence (XRF) data, observed their crystalline properties using X-Ray diffraction (XRD) patterns, peak full width at half maximum (FWHM) values. The wet etched micrographs of their cross-sections were inter-compared to show the extent of variation. Even though the XRD data of these samples are similar, the wet etched micrographs along with the Raman spectral data varied a lot from brand to brand. Effects of halides, oxygen, nitrogen impurities on its long-term corrosion and degradation of rebars is also discussed. It is suggested that better convergence of Raman spectral data for all brands of steel rebars along with their FWHM values will replicate similar microstructural images across all brands and will thus ensure better formulation of uniform quality standards across all brands and ensure higher longevity of related civil engineering structures, irrespective of the brand.

Keywords: Steel rebars; Different brands; Repeatability; Raman Spectra for standardization

1 Introduction

History of steel rebars in India is tied to the history of progress in reinforced concrete and its usage in various civil engineering projects in India. Steel rebars were earlier produced and used for protecting homes in different formats *e.g.*, in doors and windows etc. since the last several hundred years. Modern reinforced concrete has been used in Continental Europe since mid-1800s and came to India around 1900s. These reinforced concrete-based constructions were touted to last several hundred years in India, as compared to brick and mortar based traditional Indian construction which needed major repairs very two hundred years or so. Reinforced concrete's usage soon picked up pace on this premise and was initially used in roofing houses and its' pillars in South Asia. It was then progressively used in bridge pillars, and thereafter in long spanned bridges for its pillars and spans, and high-rise buildings and such other complicated modern structures. With rise in concrete usage, use of steel rebars for extra strength also increased exponentially over the last hundred years or so. As of today, approximately 35% of the annual national steel production in India are used in the form

of steel rebars for civil engineering construction. With increase in production volumes, the complexities of steel production in terms of volume, quantity and purity requirements, repeatability, existing checking methodologies, automation requirements also increased manifold. Indian steel rebar production is about 24 million tons today and contributes about Rs. 1,20,000 Crore to the Indian national economy each year. It generates employment for a big segment of the national population in different regions of the country, in direct and indirect forms. But one also needs to think of better methodologies for improving its quality and repeatability.

Steel rebar specifications in India have gone through some major changes over the years. Around 1972, the steel rebar quality specifications were changed from mild steel to stressed steel^{2,3}. This was supposed to increase the strength of the steel. Alloyed and later Hot Rolled steel rebars were introduced into the Indian market thereafter to increase the steel strength even further. Around, 1980s, the use of zinc coated steel rebars were propagated, with the stated objective of reducing corrosion in the rebars within the concrete matrix after concrete casting. In that context, International Zinc Association has been trying to promote the use of zinc coated rebars to reduce corrosion of steel rebars in concrete in India^{4,5}.

*Corresponding author: (E-mail: nkarar@nplindia.org)

In the last 10-15 years or so, effectiveness of polymeric coatings on steel rebars have also been experimented on, to observe its efficacy in reducing the corrosion of rebars inside the concrete matrix⁶. On the other hand, analysis of possible root causes of reinforced concrete degradation far inland, without any effects of the sea coast has also been done by one of the authors earlier^{7,8}. Some of the related suggestions are to be followed very carefully in the local context.

In India, the Bureau of India (BIS) has set standards for steel rebars through the notification number IS-1786:2008⁹. It is the benchmark for steel rebar quality in India. This is irrespective of the nature of coatings, and their effects as above, on the durability and long-term stability. In other spheres of human knowledge, associated technology has evolved a lot over the last 100 years. So, with changing times, and with better knowledgebase generated by mankind, and with availability of improved experimental techniques, one can have much better controls on quality and processes in all production systems. Hence there exists the possibility for improving the standards and benchmarks in steel making as well. Here, we propose how it may be implemented in future. Accordingly, we compared the X-ray diffraction patterns of steel rebars from different manufacturing brands across India, and their cross-sectional wet etch performance. We show how they differ from brand to brand. But wet etching differentiates samples only in a qualitative way. In today's analytical world, quantitative numbers are much more useful, especially if such quantitative analysis is possible at room temperature. Raman spectra was discovered about a hundred years ago. Since then, a lot of information has been collected for Raman spectra of different materials and they have been distinguished from one another. It's potential as a routine characterization tool at room temperature is now being slowly realized. Elemental composition of different rebar brands in terms of differences in impurities were first noted. Raman spectra of freshly cut cross-sections of these samples show in what way they differed. A correlation with impurities and microstructure was made. We assign a brand code for each brand during this presentation. A better methodology for quality analysis of Indian steel rebars is suggested using XRD and Raman spectra, so that in future, their performance and microstructure is much better and comparable with one another,

irrespective of the brand for ensuring better quality and repeatability.

2 Experimental

Twenty-three fresh and new samples of different Indian steel rebar brands used in civil engineering construction industry were collected from different construction sites and retailers across different parts of the country, incorporating most major regional and national brands. Cross sections were cut for fresh surfaces. Data were checked and inter-compared by repeating the measurements. Samples were also checked in polished and as is condition. Brand anonymity shall be maintained. Each brand shall be referred by their assigned codes, R-1 to R-23 respectively.

X-Ray Fluorescence (XRF) spectra related data collection and analysis was done to know the nominal elemental concentration and composition of the alloys. These were subsequently correlated with data from SEM-EDAX. A Rigaku ZSX Primus wavelength dispersive X-ray fluorescence spectrometer (WD-XRF) was used. This spectrometer has an Rh-target end-window sealed X-ray tube, operated at 4 kW as excitation source and a scintillation counter serves as the detector. It has a LiF (200) based analyser crystal and uses X-ray $K\alpha$ spectral lines for elemental analysis at a tube rating of 50 keV and 60 mA. Instrumental calibration was ensured before collection of data. To be sure of the reliability of results, the samples were also run on a different WD-XRF instrument of a different brand for confirmation of repeatability of the data.

Etching of these alloy samples were done using a modified nital solution, comprising 100 ml of 2-Propanol and 10 ml of Nitric Acid, in as is condition and both were sourced from Rankem (India) Ltd. Samples were etched for 4 minutes in each case and thereafter the reaction was stopped by decanting, flooding and repeated washing with de-ionized water. 2-Propanol was chosen as it is in better compliance with local laws. Choice and justification for the etchant used was based on literature reports¹⁰.

Morphology and elemental analysis studies through Energy Dispersive X-ray spectroscopy (EDAX) were done using a Tescan Magna GMH Field Emission Scanning Electron Microscope, having an EDAX attachment. All samples were inter-compared at a magnification of 2000X. It was operated at 15kV, 100 pA. The X-ray diffraction(XRD) analysis of our

Table 1 — shows the elemental composition profile of 23 steel rebar samples of different brands -1 to R-23 as obtained using EDAX.

Sample Name	EDAX based Composition (wt %)															
	Fe	C	O&N	Si	Al	P	S	Cl/F	K/Na	Ca	Cr	Mn	Ni	Cu	Mo	Mg
R-1	64.87	17.46	13.06					4.61								
R-2	75.53	11.66	7.33					5.49								
R-3	71.8	17.36	10.84													
R-4	66.97	19.96	8.32					4.75								
R-5	63.42	19.95	11.75					4.88								
R-6	66.72	26.69	6.58													
R-7	68.11	19.84	6.90					5.15								
R-8	76.14	14.1	4.92					4.83								
R-9	64.81	18.55	11.82					4.82								
R-10	53.45	33.58	11.56							1.41						
R-11	53.89	28.1	13.61					4.4								
R-12	76.50	13.81	4.67					5.03								
R-13	75.15	11.63	7.97					5.26								
R-14	65.97	14.46	11.89	0.24				5.68	1.75							
R-15	52.54	36.77	7.19					3.50								
R-16	63.75	30.22	6.02													
R-17	63.88	10.03	22.13					3.96								
R-18	46.84	14.58	34.79					3.79								
R-19	78.01	12.26	4.76					4.97								
R-20	80.29	13.92						4.71				1.08				
R-21	76.12	11.10	7.6					5.19								
R-22	74.72	12.98	6.71					5.59								
R-23	75.78	12.75	6.26					5.21								

samples were done using a Rigaku make (Ultima-IV) model Powder X-ray diffractometer having a copper target (1.54 Å). It was operated at 40kV and 40 mA.

Calibration of the XRD instrument was checked using powdered alumina, a certified Indian Reference material-based sample as a standard before taking the data. The step width was 0.02 and nominal scan speed was 3 degree/min. Such data obtained was not correlated with elemental data from Spark Plasma based optical emission spectrometry (SP-OES) - as it would not give information on the oxygen content of these samples, while carbon and oxygen content are some of the contentious issues here.

Raman spectra of these samples were recorded using a Renishaw in Via Raman Spectrometer, UK having a laser excitation source emitting at 514 nm, with exposure times of up to 120 or 180 seconds as per requirement. Such higher exposure times were at times needed to get better identifiable features. Raman spectral peaks were identified through a XRD phase correlation and also using literature reports on Raman spectral lines of such crystalline phases as discussed below. Detailed background subtraction was also done using Origin7.5 software and the data is shown in a more presentable format.

3 Results and Discussion

Table 1 shows in weight percentage, the elemental composition profile of 23 randomly collected samples of steel rebars, R-1 to R-23 of different brands as measured using EDAX. EDAX is not a very accurate method. However, it gives an estimation of the possible elements in an unknown sample. Table 2 shows the elemental composition profile these 23 steel rebars, as above, R-1 to R-23 using XRF in weight percentage. All elements detected were expressed upto the second decimal point. A comparison of the data from the two tables easily suggests that XRF has better ability to detect a greater number of impurities. XRF is possibly more consistent in the numbers it presents. It is known that the composition w.r.t. carbon given by EDAX is not at all reliable. The comparative numbers obtained from XRF are much more reliable. The reason for that is that in the present methodology used in WD-XRF, the X-rays pass through the sample and emission is detected on the other side. As may be seen, all samples had a good amount of carbon content. Many of the rebar samples were seen to have a good and detectable amount of oxygen and nitrogen content as well, even though the measurements were along the

Table 2 — shows the elemental composition profile of 23 steel rebar samples of different brands R-1 to R-23 as obtained using XRF.

Sample Name	XRF based Composition (wt %)															
	Fe	C	O&N	Si	Al	P	S	Cl	K/Na	Ca	Cr	Mn	Ni	Cu	Mo	Mg
R-1	100	0	0	0												
R-2	72.56	3.64	23.30	0.50												
R-3	57.65	6.82	33.62	0.25	0.70	0.02	0.07	0.16	0.02	0.13	0.16	0.26	0.06	0.06	0.02	
R-4	100															
R-5	100															
R-6	94.52			4.17						1.31						
R-7	94.04	5.96														
R-8	92.89	6.53								0.58						
R-9	89.71			5.56	2.80					1.93						
R-10	61.94	10.73	25.64	0.26	0.07	0.03	0.06	0.05	0.74	0.13	0.02	0.25		0.06	0.02	
R-11	90.55	2.98	5.16	0.36	0.11	0.01	0.04		0.02	0.05		0.72				
R-12	46.98	5.48	45.76	0.11	0.08	0.28	0.03	0.13	0.47	0.13		0.43		0.03		0.09
R-13	99.38			0.62												
R-14	75.02	4.22	18.99	0.31	0.11	0.04	0.10	0.12	0.49	0.03	0.09	0.26	0.09	0.12	0.02	
R-15	100															
R-16	100															
R-17	88.75	11.25														
R-18	60.19	11.32	26.83	0.32	0.07	0.02	0.06	0.12	0.28	0.43	0.09	0.22		0.04	0.01	
R-19	43.28	4.92	41.09	3.18	1.36	0.02	0.23	0.16	0.76	3.89		0.51				0.60
R-20	67.37	8.23	23.05									1.35				
R-21	64.33	6.50	26.57	0.61	0.48	0.07	0.11	0.08	0.31	0.28		0.45				0.21
R-22	59.40	4.57	35.07	0.20	0.07	0.05	0.07	0.02	0.05	0.05	0.04	0.35			0.02	0.05
R-23	89.75			3.90	0.99		1.73	1.12		2.51						

cross-section for all samples. Such oxides and nitrides may aid in the long-term enhancement of oxidization and degradation of the rebars in terms of strength and corrosion. In aqueous ambience, upon long time exposure, such nitrides can form corrosive nitrates and can significantly cause the wet-etching of the rebars from within. In general, carbon is used at the starting point of iron making to remove the oxygen content from the ores. However, it seems that in some of the samples, their traces have partially remained. But several manufacturers' samples showed pure iron rebars, with no impurities of Si or C, or P or of other elements (Table 2). In some cases, the detected iron content was as low as 45% or so. Now if the same instrument is able to detect in similar samples, iron with high purity, then there is possibly no reason to doubt the integrity of this data. Since such data can sound controversial, to be sure, such measurements were also repeated with polished and unpolished surfaces. Often, halogens are present in the rebars in detectable amounts. Such halogens are often known to degrade rebars in aqueous medium on long time exposure. So, degradation of the rebars can get enhanced by such constituents. They are not in the best interest of long-term stability and durability of related reinforced concrete structures. Updating BIS

standards and manufacturers' self-imposed quality control standards are in that context overdue. In addition, elemental contents like Si were present, at times upto 5.5%, carbon at times upto 11%. Hardening elements like P, S were also detected at times, upto 1.5% range. Other alloying elements were also detected at times, though in decimal points, like Ni, Mn, Cu, Mo, Mg. Salt forming elements like Na, K, Ca were often found in measurable qualities. In the long run, in aqueous ambience, such salt forming elements can contribute to the slow degradation of such steel rebars and associated reinforced concrete.

The current BIS standards used for steel rebars in civil construction, IS-1786:2008 also needs to be considered and discussed here, as most manufacturers are expected to, adhere to, implement and follow these. It has no lower bound for iron purity requirements in % terms. It gives an upper limit for carbon purity, but it seems these numbers are most of the time never respected to in letter and spirit. Presence of halides and salt containing elements in measurable quantities suggest that sources of raw materials used have not been fully checked for impurities and possibly recycled scrap steel materials may have been re-melted without removing the impurities. There is no prohibition on the presence or

absence of halides or salt forming elements or on any lower bounds set on their presence in the present BIS standard. We could not detect Ti or Nb or V in these samples. Carbon, oxygen and nitrogen content was, at

times, way above the specified limits in many of these samples⁸

Figure 1 shows the X-Ray Diffraction (XRD) patterns for eighteen of these twenty-three steel rebar

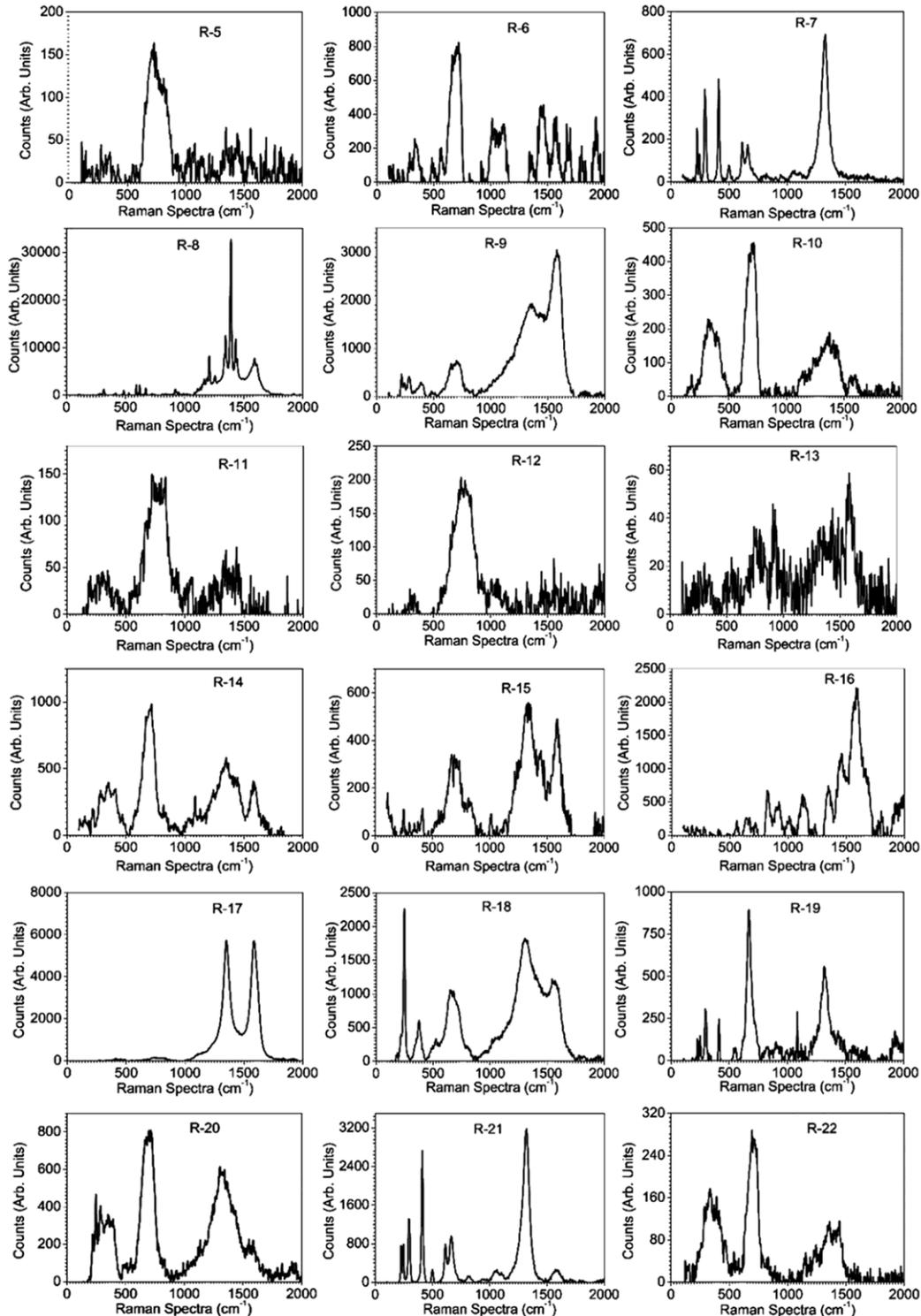


Fig. 1 — Showing the X-Ray diffraction pattern for 18 representative steel rebar samples of different brands.

samples. All the twenty-three samples' data could not be accommodated due to constraints of space. All the samples, including the ones not presented here follow the JCPDS Card No. 06-0696, based pattern, which shows a major peak at 44.67° , then at times a very small hump at 65° in general. The differences between the samples however, were in their observed peak FWHM values. The FWHM values have been marked in the individual figures. One has to remember that XRD peaks are detectable only for those components that are in crystalline form. So, iron oxides or iron nitrides that are in amorphous form are not detected by XRD. That was possibly another major contributing factor for brand-to-brand variation in quality. XRD peak positions were almost the same but the peak FWHM values varied. Hence, periodically, more stringent independent blind third-party checks, and mandatory independent accredited third-party certifications are suggested on every batch-to-batch basis, so that in the long term, the houses and buildings / civil structures do not get destroyed in fifty years or so in India. Incidentally, modern reinforced concrete structures in continental Europe have lasted more than 250 years or so. We propose a methodology and suggest the use of X-Ray diffraction peaks along with Raman spectra and their FWHM values in analysis of steel rebar samples for ensuring repeatability of microstructure and readily detecting presence of carbon and such other phase and impurity formation issues. The related results and discussions follow.

A macroscopic technique like XRD gives different FWHM values and their associated differences in microstructure and quality. As part of updating the BIS standards and specifications, the need for XRD peak intensity related 2θ values and specifications for FWHM values, including their acceptable variation should be set for better steel rebar related standardization in future.

Figure 2 shows the wet etched micrographs for the same eighteen of these steel rebar samples as above (R-5 to R-22). All these twenty-three samples' micrographs could not be accommodated due to constraints of space. Wet etching was necessary, to highlight the brand-to-brand surface morphology variation. Each of them shows different patterns, not quite the same, in terms of qualitative surface differences. A possible reason for this observation is the differences in composition in these rebars, in terms of major and minor constituents, leading to

differences in etch patterns. The carbon and different minority metal oxide constituents will not etch the same way as the main constituent iron. This also holds true for the other minority constituents alloyed with iron in several of these samples, from R-1 to R-23. Based on such etching profiles, we may differentiate the samples into three broad categories. Samples like R-1, R-3 (not shown here), R-5, R-10, R-13, R-14, R-21, R-23 show a semblance of layered, often uniform beach type sedimental formation after etching. Most of the samples in this category had an inherently lighter contrast. Such morphology could possibly indicate inherent nano-porosity inside. So their XRD FWHM values observed are different from the others. At the same time, samples like R-2, R-4, (not shown here), R-7, R-9, R-11, R-15, R-16, R-17, R-20, R-22 are of a different kind in the sense that the surfaces are plane, with no porosity at all and very little sign of any visible islandic formation. Morphology wise, we categorize this group as the best as it has no pores *i.e.* morphological features are largely absent. On the other hand, the other extreme are sample surface morphologies seen in R-6, R-8, R-12, R-18, R-19, showing islandic structures, or porosity to some extent, possibly due to presence of preferentially unetched components, possibly like silicates, carbides or oxides *etc.* in them.

Figure 3 shows the room temperature Raman spectra for eighteen of these steel rebar samples. Each of them shows eighteen different spectral patterns, none of them being quite the same. Some common traits may be seen in all of them. Raman peaks in these steel rebar cross-sections were seen in some common spectral regions like 280 cm^{-1} , 410 cm^{-1} , 700 cm^{-1} , 1315 cm^{-1} , and 1590 cm^{-1} respectively. On a sample-to-sample basis, there are slight shifts in these peak centres. The sample-to-sample variation in Raman Spectra and profile were seen in terms of relative intensity changes and changes in their FWHM values of individual peaks¹¹. A possible reason is the presence of different amounts of carbon, oxygen, and other impurities in the different iron matrices, slight difference in crystallinity and related changes in possible lattice vibrations. The peak at 280 cm^{-1} is attributable to often observed presence of Na/ K ions in these samples¹¹, the peak at 410 cm^{-1} is attributable to oxygen constituents in the matrix¹², the peak at 700 cm^{-1} is attributable to oxygen related vibrations from iron oxide^{13,14}, the peak at 1315 cm^{-1} is attributable to vibrations associated with iron (D band)¹⁵, while the

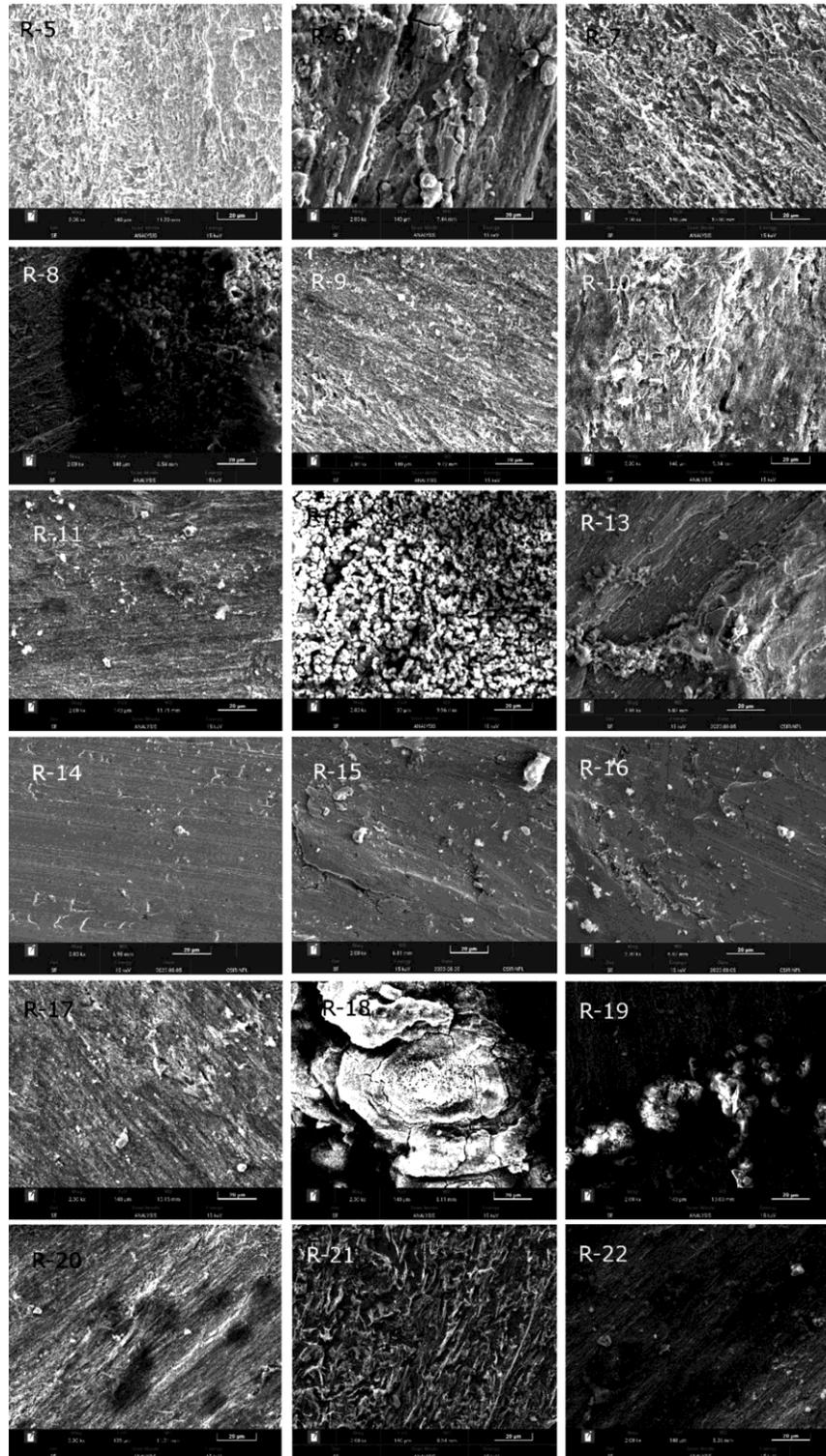


Fig. 2 — Shows the SEM images of 18 chosen representative steel rebar samples of different brands, after the samples had been etched in nital solution. Brand to brand differences now become obvious.

peak at 1590cm^{-1} is attributable to vibrations of main constituent iron but with carbon when present in graphitic form respectively based on the composition

analysis presented here. However, Hambrock *et al.* interprets the peak at 1315cm^{-1} as due to hematite¹⁵.

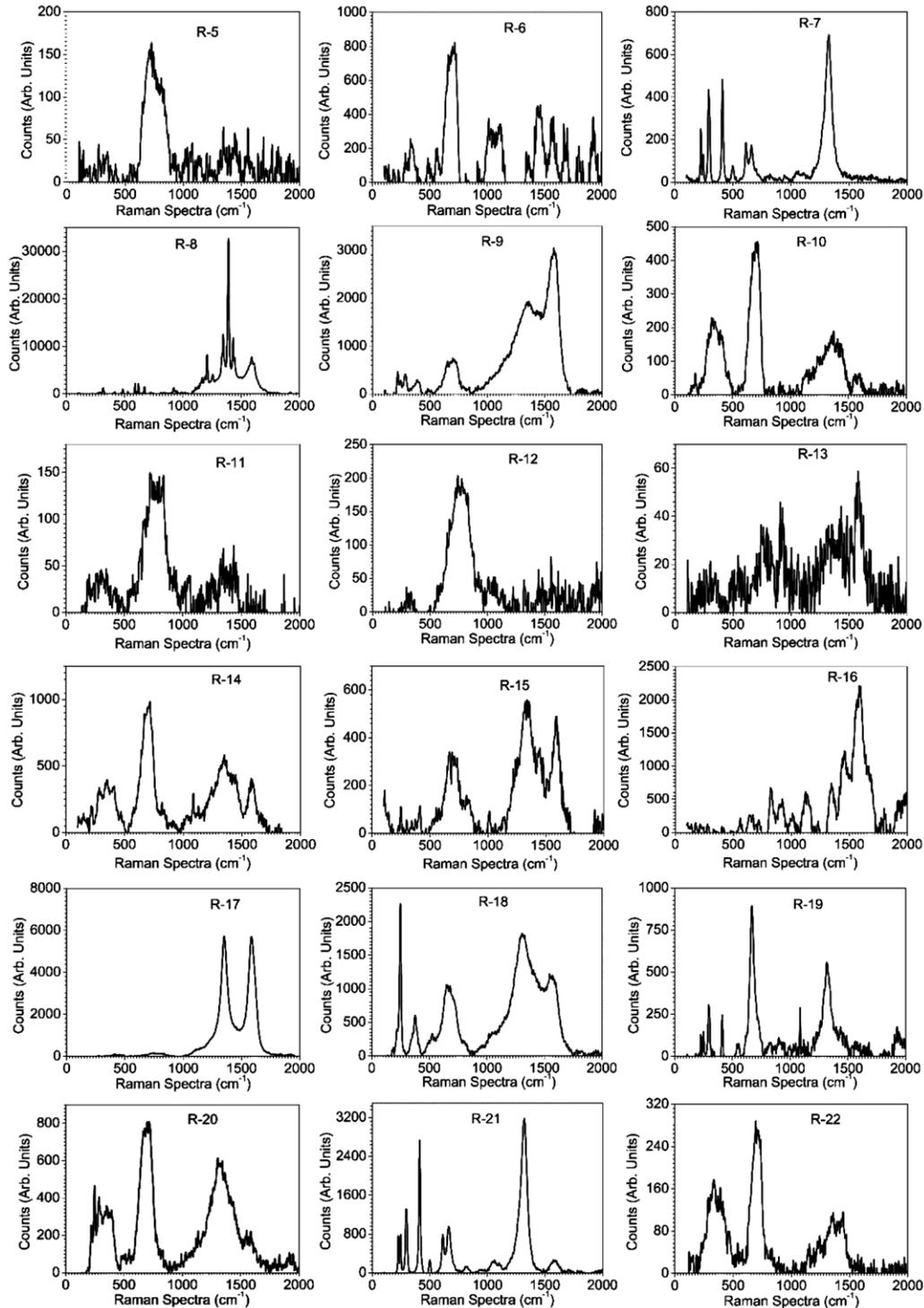


Fig. 3 — Shows the room temperature Raman spectral pattern for 18 representative steel rebar samples of different brands. No two brands had the same profile.

Some of these peaks are also seen in purer rebar samples. Moreover, even in iron carbide samples, peaks are seen in this regions¹⁷. So, this Raman peak at 1590 cm^{-1} can be associated with iron (G band).

Main peaks were stronger in intensity when the sample crystallinity and sample homogeneity was relatively better. Based on the composition analysis, ideally speaking, it may be said that Raman peaks at

1315 cm^{-1} and 1590 cm^{-1} are desirable peaks due to their association with pure iron, while the other peaks at 280 cm^{-1} , 410 cm^{-1} and 700 cm^{-1} due to oxygen, carbon and such other constituents may be classified as undesirable peaks. Their FWHM values can be easily calculated. But in a mass-produced cheap product like steel rebar, with less quality checks, we can try to limit relative intensities of smaller peaks to 5 or 10%. We may group these analysed samples into a few categories based on these observations.

In the first category are the samples that show a strong prominent peak at around 700 cm^{-1} . In this grouping are samples like R-1, R-3, (not shown), R-10, R-11, R-12, R-14, R-16, R-19, R-20, and R-22 respectively. Samples like R-8, R-9, R-16, R-17, R-21 are not in this grouping, as they have no or only moderate peaks here. The second grouping is samples that have a very strong peak at 1315 cm^{-1} -in this grouping are samples like R-7, R-8, R-15, R-17, R-18, R-20, R-21 respectively.

The third grouping is for samples that have very strong Raman peak at 1590 cm^{-1} . In this, we find samples like R-9, R-13, R-15, R-16, R-17, and R-18 to some extent. The peaks at 280 cm^{-1} and 410 cm^{-1} , if and when observed in this third group, are relatively low intensity peaks, if at all. Raman peak intensities are generally less, if the crystallinity is less or else if the related compound involved has less proportional presence in the concerned rebar matrix. As seen from above representative examples that Raman spectra is able to detect, in a quantitative way, such extent of variations in quality and composition of steel, it is hereby proposed that Raman spectra, along with its FWHM values is a good analytical technique, and is a good methodology for routine checking of steel quality, for ensuring repeatability in microstructure and for such standardization. The desirable peaks as above, and relative peak intensities that can be considered acceptable along with their acceptable FWHM values can also be framed in this manner from such data for better BIS standards in future. Along with XRD data, it is a much better and quantitative method to distinguish and segregate samples from the earlier used wet etching. Raman spectral data becomes comparable only when the crystalline structures are very similar – hence it was chosen here for bench-marking as it gives quantitative numbers.

Hence, for steel rebars, it is proposed that a representative a good standard steel rebar is one that

satisfies the JCPDS card number 06-0696, with a FWHM of 0.4 to 0.45 for each peak in terms of XRD analysis. Such a better-quality steel rebar should ideally show Raman peak intensities at 1315 cm^{-1} and 1590 cm^{-1} with FWHM values of about 70-75 cm^{-1} or so for both peaks. It will be better if only one of them is visible - the one at 1315 cm^{-1} , due to reasons like better purity, nano - crystallinity, uniformity and homogeneity. So ideally, XRD peak positions and FWHM values for JCPDS Card No. 06-0696 – and Raman spectral data with results that are reproducible as above will lead to quantification and repeatability of data to an extent that across all brands, the microstructure is repeatable and their Raman profile is very similar on a batch-to-batch basis.

European steel rebar based reinforced concrete structures have lasted a few hundred years and are still going strong. In contrast, Indian concrete generally lasts for only fifty years or so. The primary reason for concrete withering in South Asia is slow corrosion due to a host of local factors related to sand, ground water and steel^{7,8}. So better standardization of parameters for quick analysis, repeatability, and inter-comparison is essential for checking of their reliability and repeatability during production and for better long-lasting quality products. Based on above, there is possibly a need to update the present BIS [IS-1786:2008] standard.

4 Conclusion

23 different brands of steel rebars used for civil engineering construction were studied. Each of them had different chemical constituents. Often, oxygen and nitrogen were present is fairly detectible quantities along with halides. In aqueous ambience, these can easily form corrosive environments, corroding the iron at a very fast rate. Presence of carbon at higher than recommended BIS values were often detected in many of the samples. In many cases, they do not adhere to the present BIS guidelines. Composition wise, BIS standards can be further upgraded as currently there are no specifications on minimum percentage of Fe required or stricter acceptable limits for halides or oxygen or nitrogen. The observed amount of impurity content was often higher than the specified upper limit for certain impurities. The X-ray diffraction patterns for all samples were similar but their FWHM values were different. Mandatory, blind, independent third-party certification should be essential for sale of iron and steel products in the market. Raman spectra of the

cross-section of these samples were different for each of the 23 brands, though, they followed certain trends in the peak intensities, as peaks were in certain spectral regions, but their relative intensities and FWHMs were different in each case. So, there is much scope to improve the quality standards and related speciation that can be enforceable on steel rebars in the Indian context. Raman spectra can be used to routinely check the Quality of steel rebars' microstructure and their repeatability, irrespective of the brand, to the extent that it can possibly replace other methodologies currently used for analysing steel rebars.

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Data Availability Issue

Raw data from the experiments at our end are in principle available upon reasonable request and reasonable cause from the corresponding author.

Financial Interests

None of the authors have any direct financial interest in large scale commercial steelmaking as on

date. We also have no conflict of interest with any local or overseas steel maker.

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