Careful study of these phenomena leads to the suggestion, as a basis for future work, that the substances in *colloidal suspension* rather than those in more perfect solution are the first to be held back.

Fig. 3.

That this is particularly the case with asphaltic materials appears evident by the partially successful results already obtained by one of us, of precipitating asphalt from its suspension in petroleum by the presence of an electrolyte.

FURTHER REMARKS ON VANADIUM AND ITS ESTIMATION.

By GEORGE AUCHY.

Received March 16, 1909.

An important question to the steel maker who must produce steel that will stand shock and alternating stresses is, whether or not, the earnest

claim that vanadium is the best element to use to produce these qualities is a true one. Can vanadium do anything for steel that can not be done by nickel, chromium, tungsten, molybdenum, manganese, or silicon and does it outclass all these other elements in value and usefulness? The writer has made a search through the literature of the subject for an answer to this question, and while he has found an abundance of affirmative assertion, the evidence itself has been somewhat meager and contradictory evidence, that is, that bears directly on this question. Of evidence that vanadium does impart very valuable properties to steel there is no lack, and this elementary point, especially through the labors of Mr. J. Kent Smith, has received ample and complete demonstration. We need no longer ask whether vanadium is a good thing, but that it is the best thing as is so earnestly claimed, is not so clear, and as we have stated, it is to the steel maker, an interesting and important question. The writer wishes here to bring together results bearing on this point that have been quoted by him in several scattered numbers of the *Iron Age* (adding to them a few others), but expressing these results in single "quality figures" instead of in the original detailed tensile, shock, and hardness statements. These quality figures (the tensile, shock and hardness figures summed up and expressed in a single figure) were suggested to the writer by similar ones made use of by Mr. W. L. Turner in an able article in the *Iron Age* for July 2, 1908. But Mr. Turner's quality figures aim to combine only the static and dynamic properties of steel in a single figure, leaving out (perhaps properly) the hardness. Although he can not be severely (perhaps not at all) criticized for this omission, yet the general principle of his method of calculating the quality figure is obviously illogical, and his quality figures therefore are somewhat misleading. Upon reflection, it will be clear to every one that the following rule will give just results. Instead of multiplying the factors (in his method, elasticity, reduction, and alternate stress) together, as does Mr. Turner, we compare each factor separately with the same factor in some steel which we select for a standard, making the factor of the sample steel the numerator and the factor of the standard steel the denominator of a fraction. Both terms of the fraction are then divided by the least term either numerator or denominator as the case may be. Finally, after the common divisions the sum of all the numerators is

divided by the sum of all the denominators, and the result is multiplied by 100 to give a larger and more convenient figure for comparison. The standard steel need not, of course, be an actual one, but one made up of convenient round figures for the purpose. Thus for the French system, a convenient standard is elast. 50, strength 50, elong. 5, red. 5, shock 5, hardness 100, and the following example illustrates the calculation of the quality figure for a steel of 152 elast., 159.5 strength, 10 elong., 46.9 red., 0.7 shock, and 321 hardness.

$$\frac{152 + 159.5 + 10 + 46.8 + 0.7 + 321}{50 + 50 + 5 + 5 + 5 + 100} = \frac{3.04 + 3.19 + 2.00 + 9.36 + 1 + 3.21}{1 + 1 + 1 + 1 + 7.14 + 1} = \frac{21.80}{12.14} = 1.80 \times 100 = 180 \text{ Quality Figure.}$$

But an improvement can be made by cutting out some of these factors. Thus for instance, since elongation and reduction both express the same property, to use both is to give this property (ductility) double the representation it should have. Mr. Turner therefore cuts out elongation. The writer would cut out both elongation and reduction on the ground that ductility and toughness are already represented by shock test, and these figures moreover represent perhaps not ductility at all, but nothing but the amount of pearlite (or of martensite) in the steel. Indirectly these tests are a general indication of the ductility and toughness, it is true, because pearlite interferes (and martensite still more) with these qualities also; but that there is no direct connection between elongation and reduction, and ductility and toughness, we see when we consider that ductility and toughness are qualities of the steel in its normal condition, whereas elongation and reduction are phenomena occurring after the steel has been irretrievably ruined, that is, after its elastic limit has been reached and passed.

Another factor that is of no importance and must not therefore be considered in getting our quality figures is the tensile strength, for as Mr. Turner well says, "a material is practically valueless after the stresses have exceeded the yield point." We are therefore reduced to three factors, elastic limit, shock test, and hardness, and in the results of Dr. Guillet, quoted below, the quality figures given were obtained from these three factors in the manner above described. But along with these true quality figures are also given in parentheses the quality figures obtained from all six factors,

as it was thought the comparison might be of interest. In Mr. Turner's tests the quality figures are calculated from the three factors of elasticity, reduction and alternating stresses only (hardness not given) and results are therefore not comparable with the results of Dr. Guillet's tests, but only with each other.

To find then an answer to our question as to the efficiency of vanadium compared with the elements more commonly added to steel, we turn to Dr. Guillet's paper on Quaternary Steels in the *Journal of the Iron and Steel Institute* for 1906, Vol. 2, and pick out and compare vanadium nickel steels with chrome nickel, tungsten nickel, molybdenum nickel, and silicon nickel steels, using for the comparison the 3-factor (elasticity, shock, hardness) quality figures obtained as above described. Taking first quenched steels we find as follows:

QUENCHED VANADIUM NICKEL STEELS.

Composition.	Quality figure.	
C, 0.20-Ni, 6-V, 0.50.....	258	(364, 6-factor figure)
C, 0.20-Ni, 6-V, 0.70.....	79	(180, 6-factor figure)

QUENCHED CHROMIUM, ETC., NICKEL STEELS.

C, 0.20-Ni, 6-Cr, 0.50.....	257	(240, 6-factor figure)
C, 0.20-Ni, 5-Cr, 1.0.....	305	(269, 6-factor figure)
C, 0.20-Ni, 6-Cr, 1.0.....	268	(186, 6-factor figure)
C, 0.20-Ni, 5-Cr, 3.0.....	285	(305, 6-factor figure)
C, 0.20-Ni, 6-W, 2.0.....	285	(377, 6-factor figure)
C, 0.20-Ni, 6-W, 0.30.....	279	(332, 6-factor figure)
C, 0.20-Ni, 5-W, 0.30.....	284	(380, 6-factor figure)
C, 0.20-Ni, 6-Mo, 1.0.....	235	(229, 6-factor figure)
C, 0.20-Ni, 6-Mo, 0.50.....	284	(259, 6-factor figure)
C, 0.20-Ni, 6-Mo, 2.0.....	248	(237, 6-factor figure)
C, 0.20-Ni, 6-Si, 0.50.....	271	(364, 6-factor figure)
C, 0.20-Ni, 6-Si, 0.80.....	281	(380, 6-factor figure)

In the above tests, vanadium shows inferior if anything to chromium, tungsten, molybdenum, and even to cheap and common silicon. Looking for further comparisons with silicon, we obtain the following:

QUENCHED VANADIUM NICKEL STEELS.

C, 0.20-Ni, 2-V, 0.30.....	267	(347, 6-factor figure)
C, 0.20-Ni, 2-V, 1.0.....	215	(261, 6-factor figure)

QUENCHED SILICON NICKEL STEELS.

C, 0.20-Ni, 2-Si, 1.5.....	223	(155, 6-factor figure)
C, 0.20-Ni, 2-Si, 1.0.....	249	(174, 6-factor figure)
C, 0.20-Ni, 2-Si, 0.50.....	292	(239, 6-factor figure)

Indicating again the superiority of silicon, and showing also that anything over 0.50 per cent. of either element causes deterioration.

But in the tests so far quoted, it will be seen that vastly different comparisons are obtained with the six-factor figures, this because vanadium gives as a rule such high figures for reduction of area. But further reflection only serves to confirm us

in our conviction that elongation and reduction dare not be admitted into the calculation of quality figures, where shock tests also figure, because in the first place these two tests are obviously no sure indication of ductility and toughness, as has always heretofore been taken for granted (all through Dr. Guillet's tests may be found instances of steels showing 5 or 6 times the reduction of certain other steels, and yet coming the same or even lower in shock test figures) and are therefore of no positive significance, and in the second place, if they really were an indication of these qualities, so much the greater reason why they should be omitted from the calculation, since these qualities already find representation in the shock test figures. In all the following tests of Dr. Guillet, even the 6-factor figures show unfavorably to vanadium. Considering now "normal" steels (heated to 900° C. and cooled in air) we find as follows:

VANADIUM NICKEL STEELS.

C, 0.20-Ni, 6-V, 0.30.....	169	(331, 6-factor figure)
C, 0.20-Ni, 6-V, 0.50.....	170	(320, 6-factor figure)
C, 0.20-Ni, 6-V, 0.70.....	182	(324, 6-factor figure)

CHROMIUM NICKEL STEELS.

C, 0.20-Ni, 5-Cr, 1.0.....	255	(359, 6-factor figure)
C, 0.20-Ni, 6-Cr, 1.0.....	217	(336, 6-factor figure)
C, 0.20-Ni, 6-Cr, 2.0.....	260	(303, 6-factor figure)

TUNGSTEN NICKEL STEELS.

C, 0.20-Ni, 6-W, 1.0.....	202	(286, 6-factor figure)
C, 0.20-Ni, 6-W, 2.0.....	187	(321, 6-factor figure)
C, 0.20-Ni, 6-W, 6.0.....	198	(338, 6-factor figure)

MOLYBDENUM NICKEL STEELS.

C, 0.20-Ni, 6-Mo, 0.50.....	236	(417, 6-factor figure)
C, 0.20-Ni, 6-Mo, 1.0.....	227	(328, 6-factor figure)
C, 0.20-Ni, 6-Mo, 2.....	215	(343, 6-factor figure)
C, 0.20-Ni, 6-Mo, 5.0.....	200	(321, 6-factor figure)

SILICON NICKEL STEELS.

C, 0.20-Ni, 6-Si, 0.50.....	223	(412, 6-factor figure)
C, 0.20-Ni, 6-Si, 0.80.....	145	(327, 6-factor figure)
C, 0.20-Ni, 6-Si, 1.0.....	131	(309, 6-factor figure)
C, 0.20-Ni, 5-Si, 2.0.....	134	(268, 6-factor figure)
C, 0.20-Ni, 6-Si, 2.0.....	135	(236, 6-factor figure)

Here again even silicon shows superior to vanadium, but only when the per cent. silicon is not higher than 0.50. Above that a great deterioration is manifest.

All of the results of Dr. Guillet are unfavorable we see to vanadium, but we come now to results of quite a different character, those of Mr. Turner of the Vanadium Company. In these results we must calculate our quality figure from two factors only, elastic limit and alternate stresses, hardness not being given. These quality figures are not comparable with the preceding ones.

VANADIUM CHROME STEELS.

Test No.	Quality figure.	
15.....	866	(713, 5-factor figure)
17.....	771	(699, 5-factor figure)
23.....	436	(443, 5-factor figure)
24.....	500	(550, 5-factor figure)
27.....	501	(534, 5-factor figure)

NICKEL CHROME STEELS.

Test No.	Quality figure.	
21.....	437	(559, 5-factor figure)
28.....	424	(507, 5-factor figure)
9.....	545	

These results are highly favorable to vanadium; out of 5 cases, in one only is the vanadium no better than the nickel. In two others it is well above, and in the remaining two it is very far superior to most of the nickels. But in view of the contradiction given by Dr. Guillet's results, and in view also of the fact that only one percentage of nickel (1.75 per cent.) was experimented with by Mr. Turner, and no other element than nickel compared with vanadium, we must wait for further light before drawing positive conclusions.¹ However the matter may ultimately turn out, the estimation of vanadium in steel and in alloys has become a common thing with steel chemists, who may be considered as heartily in sympathy with vanadium's struggle for supremacy on account of the ease with which the element can be estimated. The great analytical authority, Mr. A. A. Blair, first separates from the iron and molybdenum by ether, then from the nickel, chromium and copper by caustic soda, then from the alkali by lead acetate, and finally determines the vanadium by reduction with hydrochloric acid, and titration in sulphuric solution with permanganate.

Mr. J. Kent Smith, the noted pioneer in everything pertaining to vanadium, determines the vanadium at once in the iron solution by oxidation with permanganate, filtration, reduction with weighed ferrous ammonium sulphate, and titration of excess with bichromate. Mr. Chas. M. Johnson, the brilliant and original young steel works chemist, also proceeds like this, but titrates with the ferrous ammonium sulphate instead of adding an excess. The last two are obviously easy and convenient methods, but involve a filtration, and the titration in neither case is so satisfactory as a permanganate titration, so that reduction with hydrochloric acid and titration in sulphuric solution by permanganate (without separating the iron) seems preferable. In detail as follows:

¹ There are results very favorable to vanadium quoted in Harbord's "Metallurgy," but not considered here because tensile exclusively.

In steel dissolve 5.12 grams drillings in a casserole in 75 cc. nitric acid, sp. gr. 1.20. If the steel contains chromium, 25 cc. strong hydrochloric acid are also added. A blank test on the same weight of some vanadium-free drillings is also made. Cover and boil, nearly dry. If the hydrochloric acid has been added, add 50 cc. strong nitric acid, and again boil, nearly dry. Remove cover and evaporate to dryness at a gentle heat. Cover and heat (the flame barely touching the plate) to decomposition of nitrates and until cover is dry. Add 150 cc. strong hydrochloric acid and boil nearly to dryness. Add 75 cc. dilute (2 to 1) sulphuric acid and evaporate, with cover off, to complete expulsion of the hydrochloric acid. Cool, take up with 300 cc. water, and again evaporate to pastiness. This second evaporation is to give any V_2O_3 all possible chance to oxidize up to V_2O_4 in recognition of Treadwell's point that strong hydrochloric acid reduces V_2O_5 to a variable mixture of V_2O_4 and V_2O_3 . Take up with 100 cc. water and heat. Transfer to a 500 cc. Erlenmeyer flask. Cool, dilute to about 350 cc. and titrate with permanganate, of iron strength 0.005585; cc. permanganate divided by 10 gives per cent. vanadium. The pink color must persist after 50 or 60 shakings of the flask. In chrome vanadium steels the permanganate used up in neutralizing the green chromium color must of course be allowed for. This may be found once for all by experiments. The writer's rule is to deduct 0.1 cc. for every 1 per cent. chromium and 0.1 additional, this for the neutralization of the green chromium color, and in addition to the regular dummy. As stated, this chromium correction may be found once for all, but not so the regular dummy. This must be made every time, or at least every time a fresh lot of sulphuric acid is used. It seems to be the sulphuric acid that is responsible for the variations in the dummy, but of this the writer cannot be sure. He has only noticed that for a long series of tests the dummy will be constant (say 1.0 cc.) and then suddenly will change to perhaps 0.7 cc. which will then persist for another series of tests and so on, so a dummy every time would seem to be safer.

In Ferro-vanadium.—Take 0.512 gram of the crushed sample, and for the dummy take 0.3 gram of any vanadium-free steel drillings. Dissolve in a dish in dilute nitric acid, adding strong hydrochloric acid. Boil nearly to dryness with cover on and add 50 cc. strong nitric acid. Boil nearly dry, lower flame, remove cover, and evaporate at a gentle heat to dry-

ness, add 25 cc. strong hydrochloric acid and boil until green, add 50 cc. water, stir up and filter. Wash alternately with hot, dilute hydrochloric acid and water. To filtrate add 1 cc. concentrated nitric acid and 50 cc. concentrated hydrochloric acid and evaporate to dryness—at a gentle heat when nearly dry. Add 150 cc. strong hydrochloric acid and boil nearly dry. Then 15 cc. dilute sulphuric acid (2 to 1) and evaporate until no smell of hydrochloric acid is perceptible, cool, add 300 cc. water, mix, and evaporate again. Take up with water and heat, transfer to a 500 cc. Erlenmeyer flask, cool, dilute to about 350 cc. and titrate with permanganate of 0.005585 iron strength. cc. permanganate equals per cent. vanadium. The residue is tested for vanadium, by burning of paper, dissolving in hydrofluoric and a little sulphuric acid, evaporating, igniting and weighing as Fe_2O_3 plus V_2O_5 . Then the V_2O_5 separated by fusion with sodium carbonate and filtration of the aqueous solution, the residual Fe_2O_3 weighed and the V_2O_5 obtained by difference.

This method of determining vanadium by reduction with strong hydrochloric acid and titration with permanganate has of course been in use from the very beginning, as it is the simplest and most obvious plan. But the general, if not the unanimous opinion has been that the iron must first be separated. From Campagne, the first one to publish a description of the method, applied to steel down to Blair, who recently has described an application of the method to steels containing molybdenum and chromium, the iron is directed to be first separated by ether. Why? The only reason the writer can see is the fact that the end point of titration cannot be distinguished with much iron present, and the liquid hot when titrated. But if the liquid be cold there is no difficulty in getting the end point of the titration. Must the liquid then be hot? The following tests with vanadium solution made in the cold seem to answer this question in the negative.

Per cent. present, by reduction with zinc to V_2O_2 form, 1.13.

Per cent. present, by mercurous nitrate method, 1.10.

Per cent. found by above described method, 1.15, 1.13, 1.15, 1.14, 1.15, 1.11, 1.13, 1.13, 1.13, 1.12, 1.13, 1.13, 1.15, 1.16.

Then a new vanadium solution was analyzed, found to contain no impurity except alkali, and the vanadium determined in an aliquot portion

gravimetrically by mercurous nitrate precipitation with the following results:

Vanadium, per cent.: 1.36, 1.39, 1.34, 1.37, 1.35, 1.36, 1.36, 1.36.

Then as above, titrating cold, per cent.: 1.35, 1.33, 1.36, 1.33, 1.29, 1.31, 1.29.

Then with iron present equivalent to a sample of steel: 1.37, 1.38, 1.39, 1.38, 1.37, 1.38, 1.36, 1.38, 1.39.

Then without iron, titrating hot: 1.37, 1.37.

The point made by Treadwell that strong hydrochloric acid reduces V_2O_5 to a variable mixture of V_2O_4 and V_2O_3 is a point that it appears has been entirely ignored by other analysts.

The above results show no indication of any such thing as declared by Treadwell, but the writer did get a series of three results—all obtained at the same time—that do corroborate Treadwell's statement, namely, 1.48, 1.52, 1.55. But evidently the error is one that occurs but rarely. To obviate it altogether, the writer can think of nothing better than to evaporate to pastiness a second time before titration, in order to give the V_2O_3 if present plenty of opportunity to oxidize up to V_2O_4 . Whether or not this precaution serves its purpose, he cannot say. He has not had any high results since its adoption.

THE FORMATION OF WHITE SCALE ON STEEL AND THE SURFACE DECARBONIZATION OF PIPE-ANNEALED STEEL.¹

By CHARLES MORRIS JOHNSON.

Received April 10, 1909.

When bars of steel are annealed in pipes, with charcoal, to produce a scale-free, frosted, metallic finish, there is frequently found at the surface of the metal a coarsely crystalline structure (H), (G) Fig. 2, that is much lower in carbon content than the remainder of the bar. Such steel will not harden file-proof on the outside. It is rejected for that reason by makers of twist drills, though this defect be so slight as to require a magnifying glass for its detection.

In pipe-annealing, the bars are put in a steel tube that is welded shut at one end. The spaces between the pieces are filled in with wood charcoal. The open end of the pipe is plugged with fire-brick, fire-clay and a disc of plate steel. A small vent hole is located at one end of the pipe to permit the escape of the large quantity of car-

bon monoxide that is generated by the reaction between charcoal and the air yet remaining in the vessel. As apparently dry charcoal often holds considerable moisture in its pores, some water vapor must also be liberated.

The superficial decarbonization (G), (H), (I), Fig. 2, is at times much more pronounced than at others. The writer became interested to investigate the process with a view to discovering the primary cause of this very objectionable feature of annealing in a closed tube.

In the first place, it was soon noted that the condition frequently exists in steel before it reaches the annealer, due to forging at too high temperatures.

Again, it was deemed possible that the scale, always existing on the steel when it is put in the pipes, might react with the charcoal to form CO_2 . Further, that the latter gas would, under the existing conditions, decarbonize the steel by the reaction $CO_2 + C = 2CO$.

To test this theory some 5/8" Rd., high carbon steel rods were placed in a porcelain tube and heated for 18 hours with a slow stream of pure, dry carbon dioxide passing through the enclosure. The following points were noted:

1st. A glittering black scale was produced on the fractured or otherwise unpolished surfaces of the bars. On fracturing the latter, a distinct ring of coarse crystals was found to exist at the margin of the fractures. This scale has a curious property of adhering in a thick, sparkling black mass on rough fractured surfaces but when polished steel is exposed, at a red heat, to the attack of CO_2 , only a black discoloration resulted. The scale referred to, proved, on analysis, to be Fe_3O_4 . This experiment showed that carbon dioxide may cause "bark" (surface decarbonization) but not to a marked enough extent to offer a satisfactory explanation.

2nd. Some pieces of the same bar were heated in a stream of pure, dry hydrogen. A frosted metallic surface was produced and also a slight "bark." Hydrogen, therefore, will decarbonize steel by forming hydrocarbons.

3rd. Next, a piece of the bar was heated in the closed porcelain tube, packed loosely with charcoal. First air was expelled, but, as the heat attained slight redness, large quantities of CO escaped at the outlet end. After an 18-hour heating, at about 750° C. to 780° C., a handsome frosted, metallic surface had displaced the black oxide and much decarbonization was noted. The carbon

¹ From a paper read at the March, 1909, meeting of the Pittsburgh Section of the American Chemical Society.